The impacts of nutrient loading on greenhouse gas exchange in floodplain fens

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Dr Andrew Skinner, from the RSPB, undertook an in depth analysis of plant species composition and abundance within Sutton and Strumpshaw Fen in September 2012. Any data from his work (section 3.2.3 and 3.2.4, as well as Appendix 1 and 2) has been correctly cited when used. Any analysis of the raw data was undertaken by myself.

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Abstract

This research quantified the impact of nutrient loading on GHG exchange within two English floodplain fens. GHG exchange was quantified in two sites of differing nutrient status under conservation management between June 2012 and September 2013 using closed static chambers. Annual reconstructed CH_4 emission (diffuse and plant-mediated) was similar between sites (18 ± 2.6 and 15 ± 1.7 g CH_4 m^{-2} yr^{-1} for nutrient-poor and nutrient-rich sites, respectively), whilst ecosystem respiration (2725 ± 10 and 3479 ± 154 g CO_2 m^{-2} yr^{-1}, respectively) and gross primary productivity (2814 ± 103 and 5039 ± 564 g CO_2 m^{-2} yr^{-1}, respectively) were significantly greater in the nutrient enriched site, translating into a significant difference in NEE (-90 ± 139 and -1560 ± 418 g CO_2 m^{-2} yr^{-1}, respectively). This difference was caused by a greater aboveground biomass at the nutrient enriched site sequestering more CO_2. PO_4^{3-} and NO_3^- were shown to be significant controlling factors on CH_4 emission and CO_2 exchange.

Ebullition was shown to be an important transport mechanism for CH_4 within floodplain fens; fluxes were within a similar order of magnitude to diffusive and plant-mediated fluxes, which has not previously been demonstrated. Additionally, shorter sampling periods (< 48 hours) result in more reliable ebullition estimates than > 48 hours due to less oxidation occurring within the funnel traps and should be used in highly productive environment such as floodplain fens.

An *ex situ* short-term (< 15 days) laboratory fertilisation study under anaerobic conditions showed significant increase in potential methanogenesis with PO_4^{3-} additions but suppression with NO_3^- additions. Anaerobic CH_4 oxidation was observed in nutrient-poor peat after 144 hours, with the greatest oxidation rates in PO_4^{3-} fertilised samples. Potential N_2O production via denitrification only occurred in samples fertilised with NO_3^- and no difference was observed in fermentation between treatments.

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Acronyms

AWS	Automated weather station
C	Carbon
CH_4	Methane
Cl^-	Chloride
CO_2	Carbon dioxide
CRM	Certified reference material
Cs	Caesium
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbon
EA	Elemental analyser
Fe	Iron
GC-FID/ECD	Gas chromatograph-flame ionization detector/electron capture detector
GHG	Greenhouse gas
GMT	Greenwich Mean Time
GPP	Gross primary production
GWP	Global warming potential
HCl	Hydrochloric acid
He	Helium
HNO_3	Nitric acid
IRGA	Infrared gas analyser
LOI	Loss on ignition
N	Nitrogen
N_2O	Nitrous oxide
NEE	Net ecosystem exchange

NNR	National nature reserve
NO_2^-	Nitrite
NO_3^-	Nitrate
NSE	Nash Sutcliffe efficiency
O_2	Oxygen
OFN	Oxygen free nitrogen
P	Phosphorous
PO_4^{3-}	Phosphate
Ppm	Part per million
pSAC	Special area of conservation
R_{eco}	Ecosystem respiration
R.Q.	Research question
RSD	Relative standard deviation
RSPB	Royal Society for the Protection of Birds.
SO_4^{2-}	Sulphate
SRP	Soluble reactive phosphorous
SSSI	Site of Specific Scientific Interest
UHQ	Ultrapure water
VGA	Vascular green area
$ZnCl_2$	Zinc chloride

1. Introduction

CO_2, CH_4 and N_2O are three of the most important greenhouse gases (GHG) that make the Earth habitable (Karl and Trenberth, 2003, Denman et al., 2007). However, anthropic activities have altered atmospheric concentrations of these gases, leading to increasing global temperatures (Denman et al., 2007). Consequently, biogeochemical and hydrological cycles are being significantly perturbed (Denman et al., 2007), with fears of increasing biogenic emissions from terrestrial and aquatic environments (e.g. rivers, lakes, wetlands, grasslands and forests). Peatlands are a natural source of GHGs owing to the hydrological conditions that are essential for their occurrence and the decomposition processes that occur within them (van Diggelen et al., 2006, Mitsch and Gosselink, 2007). Globally, peatlands cover about 4.16×10^6 km^2, approximately 3% of the Earth's land surface (Limpens et al., 2008, Kroon et al., 2010). Northern peatlands (those north of 45°N), in particular, have become a large sink for CO_2 since the last glacial maximum due to their ability to sequester atmospheric carbon (C) and accumulate organic matter as it is produced at a faster rate than it is decomposed (Hendriks et al., 2007). Northern peatlands currently store an estimated 547 Gt C (Yu et al., 2010). With global temperatures increasing due to climate change, it is feared that the C dynamics in these environments will change from net C accumulators to a net loss of C (Aerts and Ludwig, 1997, Eriksson et al., 2010).

Peatlands can be subdivided into bogs and fens depending on hydrological inputs (van Diggelen et al., 2006). A bog is an ombrotrophic peatland that is completely dependent on precipitation for water and solute inputs, whereas fens are peatlands that receive water predominantly from groundwater, as well as surface water and precipitation, thus resulting in higher solute inputs (van Diggelen et al., 2006, McBride et al., 2011). Floodplain fens, however, are lowland peatlands that are predominantly fed by surface water, although still have some groundwater and precipitation inputs. Floodplain fens have varying nutrient status depending on the catchment of the surface water inputs, with nutrient concentrations controlling microbial activity and plant growth rate. Floodplain fens include both natural fens dominated by sedges, reeds and grasses and semi-natural 'fen meadows' and 'wet grasslands' (van Diggelen et al., 2006) and occur throughout the tropical and temperate regions (van Diggelen et al., 2006, Lähteenoja et al., 2009, Couwenberg et al., 2010).

Globally, the areal extent of floodplain fens is not known and is a current knowledge gap in the literature, with peatlands only recently being found in the Amazonian floodplains

(Lähteenoja et al., 2009). However, their importance with relation to GHG fluxes is thought to be great due to the high nutrient concentrations that these environments receive owing to their downstream, lowland location. In Europe, fens are the predominant type of peatland, covering 78% of the total peatland area of 515,000 km^2 (Bain et al., 2011). In the UK, peatlands cover an approximate 46,000 to 77,000 km^2, of which 95 % are bogs (Bain et al., 2011). Due to this greater extent, most of the C and GHG flux measurements from UK peatlands to date have been focused on upland blanket bogs (Dalrymple et al., 2011). However, it is believed that the extrapolation of GHG fluxes from these environments to floodplain fens may not be reliable because of the greater biogeochemical heterogeneity in fens and uncertainty in peat depths (Natural England, 2010, Dalrymple et al., 2011), which has an impact on rates of GHG production. Worrall et al. (2011) modelled GHG fluxes in the UK and estimated that despite covering a smaller area, 54% of the total GHG efflux from UK peatlands originates from English lowland peats. Currently, little research has been published on GHG emissions from UK lowland peatlands and is a missing link in our understanding of UK peatland C and N dynamics. Only a number of studies have been undertaken within Europe, primarily in the Netherlands and in Germany (Augustin et al., 1998, Hendriks et al., 2007, Kroon et al., 2010). However, these studies are not numerous and more research is needed, especially within the UK context.

In addition to the lack of knowledge on GHG exchange in UK floodplain fens, relatively little is known about spatial and temporal variation in ebullition, the episodic and steady release of CH_4 bubbles. Until recently, methodological drawbacks have prevented the study of the process but more recently it has been shown to be an important transport mechanism of CH_4 to the atmosphere (Glaser et al., 2004, Tokida et al., 2007, Stamp et al., 2013). No previous study has quantified temporal variation in ebullition *in situ* in a floodplain fen, nor are the magnitude of fluxes known. Thus the importance of this transport mechanism in floodplain fens is still unclear and needs studying.

The effects of nitrogen (N) and phosphorous (P) loading via fluvial inundation on peat has not been researched. With the intensification of the hydrological cycle being hypothesised due to climate change, leading to long periods of drought with episodic flooding events within north west Europe (Huntington, 2006), floodplain areas could be flooded under current UK and EU flooding policies (Defra, 2005, Lamers et al., 2006). The effects of such inundation with nutrient-rich water has not yet been researched and subsequent alterations to biogeochemical cycles and GHG exchange is not known. A

number of long-term (> 1 year) N and P fertilisation studies have been conducted on peatland environments to simulate atmospheric nutrient deposition (Keller et al., 2005, Lund et al., 2009b, Mueller et al., 2013, Nelissen et al., 2014); however, nutrient inputs over a shorter-time period (< 1 year) via fluvial inundation have the potential to be significantly greater than atmospheric deposition, especially in agricultural catchments. The importance of such perturbations to peatland C and N dynamics due to nutrient loading via fluvial inundation needs to be researched as to inform flooding policy and reduce GHG emissions to the atmosphere.

The aim of this thesis is to ascertain the impacts of nutrient loading on GHG exchange in floodplain fens. In order to achieve this research aim, a 16 month sampling period quantified GHG exchange *in situ* in two floodplain fen sites of differing nutrient status as fluxes from these environments are currently unknown in the UK and they are thought to be highly productive environments. From the field data, annual C exchange will be calculated using interpolation modelling techniques, as well as investigating the controlling factors on C exchange. A short-term (< 15 days) laboratory microcosm fertilisation experiment will be undertaken under anaerobic conditions to elucidate alterations to mineralisation processes. This will provide insight into how mineralisation processes change under short-term (< 15 days) nutrient alterations. Chapter 2 provides a literature review on GHG exchange within peatlands, focusing on floodplain fens and the current knowledge on N and P alterations to mineralisation processes and vegetation (section 2.3.4). The research questions and their respective hypotheses are outlined in section 2.5. Chapter 3 outlines the difference in nutrient status between the two chosen sites. *In situ* C exchange at the two floodplain fen sites is then reported in chapter, including temporal variability in CO_2 exchange and CH_4 emissions from the fens and ditches. CH_4 emissions via ebullition from the two floodplain fen sites are then presented in chapter 5. Chapter 6 details modelling methods used to evaluate and results from controlling factors on C exchange, annual fluxes, and global warming potentials of each site and the relative importance of fen and ditch C exchange. Chapter 7 reports the laboratory microcosm experiment used to ascertain the impacts of nutrient loading on mineralisation processes within peat substrate. Chapter 8 concludes the thesis, synthesising the key findings from this study and suggesting further research ideas.

2. Literature review

This section reviews the current literature on greenhouse gas (GHG) exchange in floodplain fens and the influence of macronutrients (specifically nitrogen (N) and phosphorous (P) species) on GHG fluxes. The review begins with an outline of GHG exchange (section 2.1), followed by an introduction to peatlands, with special attention paid to floodplain fens, in section 2.2. The carbon (C) and N cycles are then presented in section 2.3, along with biotic and abiotic controls on GHG exchange (section 2.3.3) and the interactions between C, N and P cycles in section 2.3.4. Section 2.4 provides a summary and synthesis before section 2.5 outlines the research questions.

2.1 Greenhouse gases

GHGs are naturally present in the atmosphere and make the Earth habitable, absorbing incoming and outgoing radiation (Karl and Trenberth, 2003). The main GHGs are water vapour, CO_2, CH_4 and N_2O, which are produced naturally in the bio- and hydrospheres (Forster et al., 2007). Human activities have, however, increased concentrations of CO_2, CH_4 and N_2O since pre-industrial times (Karl and Trenberth, 2003, Forster et al., 2007). All three anthropic GHGs have positive radiative forcings, a measure of the change in net irradiance (incoming minus outgoing radiation); +1.791, +0.504 and +0.175 W m^{-2} for CO_2, CH_4 and N_2O, respectively. The positive radiative forcings result in an increase in absorption of radiation and increased atmospheric warming (Forster et al., 2007, NOAA, 2011).

The most abundant anthropic GHG in the atmosphere is CO_2; with concentrations surpassing 400 ppm in May 2013 (Le Quéré et al., 2014), an increase of 44% since pre-industrial revolution concentrations (Karl and Trenberth, 2003, Denman et al., 2007, WMO, 2011). Atmospheric CO_2 concentrations grew at an annual mean rate of 4.1 ± 0.1 Gt C yr^{-1} from 2000 to 2005, a significantly higher rate than in the 1990s (3.2 ± 0.1 Gt C yr^{-1}) (Denman et al., 2007). Once emitted into the atmosphere, CO_2 has a lifetime of 30 to 95 years until it is taken up into the terrestrial biosphere or oceans or used in chemical reactions within the atmosphere (Jacobson, 2005, Forster et al., 2007, Archer et al., 2009).

Atmospheric CH_4 concentrations have increased at an even greater rate than CO_2; 158 % from ~700 ppb to ~1808 ppb, at its highest recorded in 1999 (Denman et al., 2007,

WMO, 2011). In the period between 1960 and 1999, atmospheric CH_4 concentrations increased at a rate six times faster than any other 40-year period previously (Denman et al., 2007). However, from 1999 to 2007 there has been a general decrease in atmospheric concentrations, although the processes driving this reduction are not well understood (Forster et al., 2007, Kirschke et al., 2013). Since 2007, CH_4 concentrations have been steadily increasing and reached 1799 ± 2 ppb in 2010 (Kirschke et al., 2013). The atmospheric lifetime of CH_4 is only approximately 12 years due to its removal by hydroxyl free radicals that are photochemically produced in the atmosphere (Forster et al., 2007).

N_2O concentrations have increased by 20 % since pre-industrial revolution, from ~270 ppb to ~323.2 ppb (Denman et al., 2007, Forster et al., 2007, WMO, 2011). From 1960 to 1999, atmospheric emissions grew at a rate twice as fast as any other 40 year period previously and have been increasing at a rate of 0.26% yr^{-1} since (Denman et al., 2007, Forster et al., 2007). N_2O has an atmospheric lifetime of 114 years (Denman et al., 2007).

Wetlands are a natural source of GHGs owing to the hydrological conditions that are essential for their occurrence, and the decomposition processes (section 2.3) that occur within them (Mitsch and Gosselink, 2007). Peatlands are a type of peat-producing wetland, formed by partially decomposed vegetation in waterlogged areas (van Diggelen et al., 2006). Globally, peatlands cover about 4.16 x 10^6 km^2, approximately 3% of the Earth's land surface (Limpens et al., 2008, Kroon et al., 2010). Northern peatlands (those north of 45 °N), in particular, have been a large sink for CO_2 since the last glacial maximum due to their ability to sequester atmospheric C as organic matter (OM) accumulates (Hendriks et al., 2007). Northern peatlands currently store an estimated 547 Gt C (Yu et al., 2010). Depending on a number of conditions – including vegetation and hydrology - peatlands can be a significant source of CO_2 due to the aerobic and anaerobic decomposition of OM (Veenendaal et al., 2007). Human interactions with peatland over the past two centuries have often significantly altered natural conditions and turned peatlands from being natural sinks to sources (Morris et al., 2000), such as by drainage and peat harvesting. For example, drainage of a Finnish minerotrophic fen increased GHG emission, with CO_2 emission from 623 to 1319 g CO_2 m^{-2} yr^{-1} in the adjacent virgin fen to 696 to 1319 g CO_2 m^{-2} yr^{-1} in the drained fen (Martikainen et al., 1995b). Drainage also increased N_2O emission from < 0.01 g N_2O m^{-2} yr^{-1} to 0.44 g N_2O m^{-2} yr^{-1} in the virgin and drained fens, respectively (Martikainen et al., 1995b). Drainage, however, decreased CH_4 emissions from 56 to 0.05 g CH_4 m^{-2} yr^{-1} for the virgin and

drained fens, respectively (Martikainen et al., 1995b). With global temperatures increasing due to climate change, it is feared that peatlands will change from net C accumulators to a net emitters of GHGs (Aerts and Ludwig, 1997, Eriksson et al., 2010).

Owing to the waterlogged conditions necessary for peat formation and maintenance (section 2.2.2.2), peatlands can be significant sources of CH_4. The anaerobic conditions caused by saturated substrates promote methanogenesis (section 2.3.1.1), resulting in peatlands being one of the largest natural source of CH_4 per year (Coulthard et al., 2009). Global warming potential (GWP) is a relative measure of how much heat a GHG traps on a per molecule basis in the atmosphere relative to CO_2. Atmospheric CH_4 and N_2O have GWPs 25 and 298, respectively, times greater than CO_2 over a 100 year period on a per molecule basis (Forster et al., 2007). However, despite their greater potential to trap heat, CH_4 and N_2O are less abundant within the atmosphere. CO_2 is still the GHG which is contributing the most to the greenhouse effect.

2.2. Description of floodplain fen environments

Floodplain fens have varying nutrient status depending on their catchment, with nutrient availability controlling microbial activity and plant growth rate. Floodplain fens include both fens dominated by sedges, reeds and grasses and 'fen meadows' and 'wet grasslands' (van Diggelen et al., 2006), and they occur throughout tropical and temperate regions (van Diggelen et al., 2006, Lähteenoja et al., 2009, Couwenberg, 2011).

Globally, the areal extent of floodplain fens is not known and is a current knowledge gap in the literature. For example, it was only recently found that Amazonian floodplains harbour peatlands (Lähteenoja et al., 2009). GHG exchange within tropical and temperate floodplain fens will, however, differ due to the nature of the environments (Chimner, 2004, Hirano et al., 2009). Tropical systems have higher C and N turnover rates due to greater temperatures in comparison to temperate fens (Chimner, 2004). Tropical fens are also often forested and have greater labile C and nutrient inputs, leading to greater uptake of CO_2 via gross primary production (GPP) and CO_2 emission via ecosystem respiration (R_{eco}) (Lähteenoja et al., 2009). CH_4 emission has generally been shown to be smaller in tropical peatlands than in temperate sites, possibly due to pneumatophores oxidising the substrate and suppressing methanogenesis (Couwenberg et al., 2010).

Temperate floodplain fens may be important in relation to GHG fluxes, due to the high nutrient concentrations that these environments receive owing to their downstream, lowland location, causing greater C and N mineralisation rates (section 2.3.4.2). Currently, relatively little empirical research has been published on GHG emissions from English lowland peatlands, and relatively few studies globally. Morrison et al. (2013) studied CO_2 exchange within an intensively cultivated fen, showing significant losses of C. Large areas of lowland fens in England are either under cultivation or conservation management. There has been a recent drive to return parts of the degraded, formerly cultivated, peat back to their former natural state (van Diggelen et al., 2006, Posa et al., 2011), although little is known about the impacts of fen restoration on GHG exchange, nor the magnitude of fluxes within conservation management sites. There is a real need to quantify GHG exchange within floodplain fens under conservation management in order to inform management strategies and restoration, as well as to inform future policy and adaptation for climate change. Most studies within floodplain fens have been undertaken within Europe, primarily in the Netherlands and in Germany (Augustin et al., 1998, Hendriks et al., 2007, Kroon et al., 2010). However, these studies are not numerous and more research is needed, especially within the UK context.

2.2.1 Hydrology

Hydrology is the main control on formation and maintenance of floodplain fens (Mitsch and Gosselink, 2007). Floodplain fens are predominantly fed by surface water via bank seepage and overbank flooding (van Diggelen et al., 2006), although groundwater and precipitation also play a role in a fens' hydrological inputs. Due to these hydrological inputs, floodplain fens generally have water tables at the peat surface or above. This has an impact on GHG exchange, controlling plant species occurrence and abundance, rates of respiration and fermentation, methanogenesis and rates of methane oxidation, denitrification and GHG transport to the atmosphere.

A floodplain fen's water level depends greatly on the fens location and generally varies temporally. Some floodplain fens experience daily flooding from rivers that are influenced by tides (Wösten et al., 2006, Mitsch and Gosselink, 2007). Seasonality also plays an important role in floodplain fens. Generally, the fens flood during the winter months when there is increased precipitation and river flows. Nevertheless, floods occur throughout the year during periods of high flow. During the spring and summer growing seasons, water levels are drawn down by evapotranspiration and by plant uptake of water, potentially increasing heterotrophic respiration and decreasing methanogenesis.

With the intensification of the hydrological cycle forecast by climate models (Huntington, 2006), floodplain fens could undergo more frequent and/or severe droughts and floods. These conditions may have a great impact on the natural functioning of floodplain fens, especially with government policies in the UK and Europe advocating the flooding of lowland environments during periods of inundation as to protect human settlements (Defra, 2005, Lamers et al., 2006). It is important to understand the hydrological regime of floodplain fens under conservation management in the UK and how alterations to this regime impact on GHG exchange in order to best adapt management practices to limit the effects of climate change.

2.2.2 Ecology

Floodplain fens are unique environments that provide a transitional zone between terrestrial and open-water aquatic ecosystems (Mitsch and Gosselink, 2007). The vegetation found in floodplain fens has adapted to survive in saturated, anoxic conditions (section 2.2.2.1) and is also necessary for the maintenance of these environments through the production of litter and its subsequent decomposition (section 2.2.2.2).

2.2.2.1 Vegetation

Floodplain fens, like many other wetlands, are characterised by a number of stresses that prevent many plant species from growing in these environments, such as N and P limitation (see section 2.3.4) and anoxia (Mitsch and Gosselink, 2007). Reduced oxygen availability in the rooting zone caused by waterlogged conditions prevent colonisation by many different plant species (Mitsch and Gosselink, 2007). However, many peatland plant species have morphological structures, called lacunae or aerenchyma (Chanton, 2005, Bodelier, 2011), that enable the transport of oxygen to the roots and rhizosphere. These structures support aerobic respiration and protect plants from phytotoxins by diffusing excess oxygen into the rhizosphere (Koncalova, 1990, Mitsch and Gosselink, 2007).

Plant species found in floodplain fens range from mosses to sedges, such as *Carex spp.* and *Cladium mariscus* (L.) Pohl (1809), and reeds and grasses, including *Phragmites australis* (cav.) Trin. Ex Steud. (1841)*, Phalaris arundinacea* L. (1753)*, Glyceria maxima* (Hartm.) Holmb. (1820) and *Calamagrostis spp.* Such plants are affected by the

physicochemical conditions that prevail, but also have the ability to affect these peatlands, through altering the C balance by net primary productivity. Floodplain fen plants sequester C through photosynthesis, which accounts for 0.1 to 0.5 Pg CO_2-C yr^{-1} being taken up in northern peatlands (Roulet et al., 2007).

The majority of plant growth within floodplain fens starts in early spring, although this varies between species. Peak biomass is generally reached by September, where maximum GPP generally occurs, and then dies back. With the onset of senescence, many floodplain fen plants produce above- and below-ground litter that is available to be decomposed aerobically or anaerobically (section 2.3.2.1), as well as accumulating as peat (section 2.2.2.2) during the decompositional process. For most species there is little living aboveground biomass during the winter months to preserve energy due to reduced temperatures and photosynthetically active radiation (PAR) for photosynthesis. There are, however, a number of species that have developed with evergreen properties, including *C. mariscus* and *Juncus spp.* (Wilson et al., 2007b).

2.2.2.2 Peat accumulation

Peat is partially decomposed OM that accumulates when inputs of plant litter exceed losses by decomposition, leaching and erosion (Mitsch and Gosselink, 2007). The waterlogged zone of a floodplain fen allows for OM to accumulate at a faster rate than it is decomposed, due to the high water levels throughout the year that promote anoxic conditions and anaerobic metabolism. Aerobic decomposition, the faster process, cannot take place in saturated substrates as the pore spaces in the substrate are filled with water, reducing oxygen diffusion rates by an estimated 10,000 times (Mitsch and Gosselink, 2007).

C is sequestered by plants through photosynthesis and stored as living biomass. When the vegetation starts to die back, plant litter is transferred to the peat substrate either at the peat surface (aboveground biomass) or at depth (belowground biomass). OM decomposes slowly in the saturated anoxic zone (section 2.3.1.1), acting as a reactant source for a number of microbial processes that slowly decompose the OM through processes of oxidation and reduction (section 2.2.3.2). The transfer of litter into the anoxic zone results in C originally fixed from the atmosphere by vegetation being placed into long-term storage in the peat (Hendriks et al., 2007). If inputs of litter exceed losses, peat accumulates.

2.2.3 Chemistry

The porewater, surface water and peat chemistry in a floodplain fen affect biogeochemical cycling and the redox potential, and have a dramatic impact on plant and microbial populations and processes. Most plants in fens are N and/or P limited (Wassen and Olde Venterink, 2006), impacting on plant growth (section 2.3.4.1) as well as decomposition (section 2.3.4.2). Anthropic alteration of peatland hydrochemistry and peat chemistry can have a dramatic impact on vegetation and microbes.

2.2.3.1 Nutrient inputs

Atmospheric deposition and fluvial inundation are the two main input pathways for nutrients into floodplain fens. Nutrient-rich water enters the fens via the latter process either by overtopping the river banks or through bank seepage. The effect of fluvial inputs of nutrients on GHG exchange in floodplain fens has not been quantified and could potentially alter respiration, GPP, methanogenesis and denitrification. N and P inputs via atmospheric deposition have been shown to increase rates of respiration, fermentation, methanogenesis and denitrification in floodplain fen peat (Aerts, 1997a, Aerts and de Caluwe, 1999). Furthermore, the increase in nutrients allows the growth of microbial biomass and greater activity (section 2.3.4.2). Nutrient inputs via fluvial inundation are anticipated to be greater than atmospheric deposition within agricultural catchments, which floodplain fens often are within. Little is known about how N and P alter respiration, fermentation, methanogenesis and denitrification and it needs to be further investigated.

In addition, nutrient enrichment via fluvial inundation can lead to the immobilisation of nutrients by microbes incorporating the macronutrients into their own cells to grow and resulting in the macronutrient no longer being bioavailable to plants and thus limits growth (Qualls and Richardson, 2000, Sheppard et al., 2013). Depending on C:N:P ratios, microbes will immobilise N and P by incorporating the macronutrients into their cells, until critical C:N:P ratios are reached (Wang et al., 2014b). There is no long-term study which has clearly identified critical microbial C:N:P ratios in peatlands (Wang et al., 2014b); however, Moore et al (2011) found critical C:N and C:P ratios of ~40 and ~1000 in Canadian forest litter. Sediment-associated nutrient inputs can cover lower lying vegetation and prevent normal photosynthetic activity from occurring, either putting stress on the covered plant or causing it to die (Blom, 1999). Nutrient loading can also reduce plant diversity due to increasing growth rate and taller plants, such as *P. australis*,

reducing light levels to lower lying vegetation (Güsewell et al., 2005, Olde Venterink et al., 2006) and causing some fens to lose endangered species. Little research has been done on alterations to plant dynamics caused by flood events with nutrient-rich water and needs more research to better understand and to help manage sites during and post-flood events.

With the increase of anthropic inputs of N and P into aquatic environments since the industrial revolution, and the subsequent flow into floodplain fens by surface water flooding and atmospheric deposition, increased N and P contents within the peat profile may have occurred. Increases in nutrient loads in rivers due to agriculture and sewage (Neal et al., 2005, Neal et al., 2010) alter the nutrient status of a fen, which can impact on floristic composition and richness (Raulings et al., 2010). Elevated concentrations of NH_4^+ from fertilisers have been found in aquatic environments in agricultural catchments (Min et al., 2011), which can lead to the acidification of floodplain fens (Aerts and de Caluwe, 1999), altering floristic composition and aggravating normal microbial functioning (section 2.3.4) (Ouyang et al., 2008). However, within the past two decades, N and P inputs from industrial and sewage effluents have reduced dramatically thanks to improvements in treatment processes (Jarvie et al., 2002, Neal et al., 2010). P-stripping by sewage treatment works has reduced P inputs into river by up to 95 % (Jarvie et al., 2002, Neal et al., 2010). Despite this reduction in P inputs, many lowland peatland sties still have a legacy of P inputs within the peat profile (Haycock and Lamberth, 2000, Surridge et al., 2007).

2.2.3.2 Redox conditions

As a result of saturated conditions in the peat, anaerobiosis occurs. These anaerobic conditions have an impact on chemical transformations that occur in the decomposition process, as oxygen is no longer present as an electron acceptor (Figure 1). Thus a sequence of ions; NO_3^-, manganese (Mn^{2+}), iron (Fe^{2+}) and sulphate (SO_4^{2-}); are used as electron acceptors in the oxidation and reduction processes that lead to the production of N_2O, CO_2 and CH_4 (Figure 1) (Conrad, 1996).

The supply of oxygen to the roots and rhizomes via specific plant species' aerenchyma allows aerobic metabolic functioning, as well as protecting against phytotoxins, such as hydrogen sulphide (Koncalova, 1990, Mitsch and Gosselink, 2007). Any excess oxygen is diffused from the plant's roots and rhizomes into the surrounding substrate (Mitsch

and Gosselink, 2007). This oxidises the rhizosphere (Figure 1), allowing for the mineralisation of organic C, N and P to take place. The oxidised rhizosphere also enables the production of CO_2 by either heterotrophic respiration (section 2.3.1.1) or the oxidation of CH_4 (section 2.3.1.1) by low affinity methanotrophic bacteria (Hornibrook et al., 2009). Nitrification (section 2.3.1.2) can also take place, increasing NO_3^- concentrations for denitrification to take place if there are any water-filled pore spaces supporting denitrifiers, or NO_3^- can be used by the vegetation for growth.

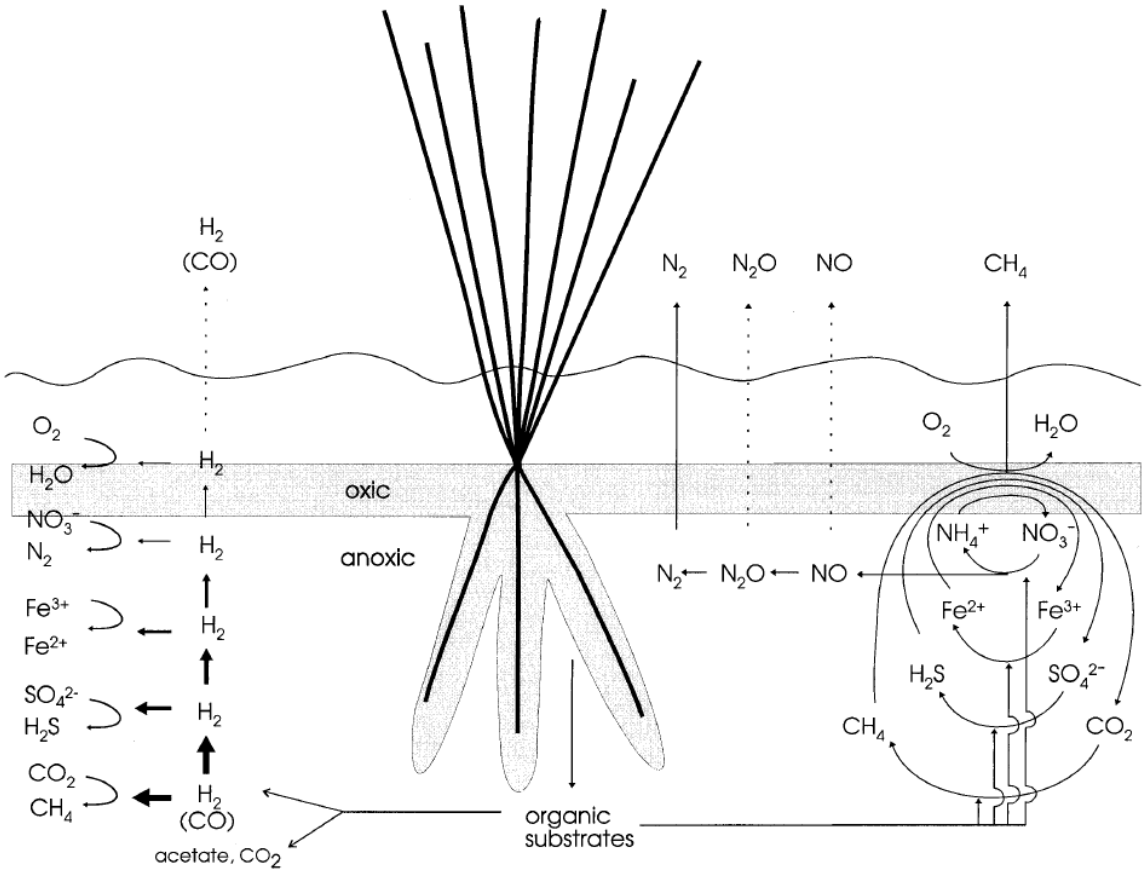


Figure 1 Conceptual scheme of the vertical distribution of different redox reactions influencing CO_2, CH_4 and N_2O production (Conrad, 1996, p. 620). After inundation of the peat substrate, a sequence of transformations take place, beginning with the depletion of oxygen, followed by the reduction of NO_3^- (to NO, N_2O and N_2, depending on pore space oxygen levels), manganese, iron (from ferric to ferrous), sulphate (to hydrogen sulphide) and finally CH_4 is produced. Throughout these reactions, the organic substrate acts as an electron donor for these processes to occur.

2.2.3.3 Reactants

The OM that accumulates as peat acts as a source of energy for many microbial processes (Rovira and Vallejo, 2002, Biasi et al., 2005). However, OM quality can influence microbial processes and have an impact on plant growth and GHG production (Rovira and Vallejo, 2002, Biasi et al., 2005). More recalcitrant OM, such as lignin, requires more energy to be processed and thus takes longer to be mineralised by k-strategist microbes; microbes that decompose more recalcitrant OM (Ryan, 1991). More labile forms of OM, such as carbohydrates and proteins, are mineralised more quickly by r-strategist microbes. Within a peat profile, more labile forms of OM are found closer to the rooting zone of plants, where plant exudates and dead roots can be found (Ström et al., 2003). Plant exudates act as sources of C but are affected by light, with greater amounts of labile C exuded with greater photosynthetic activity (Ström et al., 2003). Deeper peat is generally made up of more recalcitrant OM. Biasi et al. (2005) found that mineralisation of recalcitrant compounds increased with temperature increases in arctic tundra. Thus with increasing global temperatures due to climate change, more recalcitrant OM in deeper peat has the potential to be mineralised at a faster rate by k-strategist microbes (section 2.3.1.1), causing greater emission of CO_2 and CH_4.

2.2.4 Human impacts

Humans have had a large impact on floodplain fens. In the UK, these environments are not a natural environment, but an environment sustained over centuries after the felling of woodlands with settlement of these lowland areas (Bennett et al., 1990, Williamson, 1997). Over the centuries, cultivating the land and grazing by livestock has prevented climatic climax vegetation being achieved and the poor drainage in these areas has enabled the production of substantial peat deposits (Williamson, 1997, Wells and Wheeler, 1999). Since medieval times when it was discovered that peat was a fuel source, floodplain fens were cut for the peat to be used as fuel, resulting in the landscape present today (Lambert et al., 1960, Williamson, 1997). Within Europe, many lowland peatlands have also been converted into agricultural land, especially within the past 60 years, or have had the peat extracted to be used as fuel (Hughes and Heathwaite, 1995, van Diggelen et al., 2006). This has led to massive habitat loss, as well as a loss of a C sink (van Diggelen et al., 2006). Natural-England (2010) have estimated that 99% of UK peatlands have been degraded over the past century either by agriculture, pollution, drainage, burning or peat extraction.

Changes to a fen's hydrology can have catastrophic consequences, as they are especially sensitive to relatively small changes in water level (van Diggelen et al., 2006). Drainage of a fen and its surroundings, as well as groundwater extraction, are two of the main threats to a fen's hydrology. A reduction in water level alters the importance of rainfall as a hydrological and nutrient input into fens and the subsequent acidification from the atmospheric deposition of N and C (Aerts and de Caluwe, 1999, van Diggelen et al., 2006, Min et al., 2011). Acidification of peat occurs due to an increase in NH_4^+ concentrations, as well as the deposition of carbonic acid in precipitation that forms through the absorption of atmospheric CO_2 in rain, aggravating normal microbial functioning (Ouyang et al., 2008, Min et al., 2011).

Alterations to floodplain fens' chemistry have also occurred due to human activities. Water-level drawdown allows mineralisation to occur more quickly (van Diggelen et al., 2006), as aerobic mineralisation takes place at a rate 2.5 times faster than anaerobic mineralisation (Moore and Dalva, 1997, Frenzel and Karofeld, 2000). In turn there is an increase in bioavailable nutrients leading to an increase in plant and microbial biomass production (van Diggelen et al., 2006). Human activities have also affected the ecology of floodplain fens. The removal of the above-ground biomass to use as fuel or a building material reduces litter inputs and hence impacts on peat accumulation rates (van Diggelen et al., 2006).

More recently, it has been recognised that floodplain fens are among the most species-rich and productive habitats in temperate environments and there has been a push to conserve these important environments (van Diggelen et al., 2006, Mitsch and Gosselink, 2007). A number of governments and organisations are trying to establish or re-establish the abiotic conditions of floodplain fens to promote plant and microbial growth (van Diggelen et al., 2006), as well as the benefits associated with these. Many sites have become protected under national laws and have management practices to ensure the maintenance of these environments, while degraded sites are being restored to their former state (van Diggelen et al., 2006, Posa et al., 2011).

Floodplain fens under conservation management are subject to significant management of the sites in the UK. Frequently, the water levels within these sites are manipulated using a network of sluice gates and ditches to ensure high water tables throughout most of the year to enable normal fen functioning (Acreman et al., 2007, Strudwick, Pers.

comm.). Additionally, the vegetation is often managed, either through cutting on a specific rotation or by grazing (McBride et al., 2011). These methods are employed to maintain vegetation dynamics, reduce dominance by tall aggressive plant species and prevent succession into fen carr (McBride et al., 2011). Catchment management is also starting to be considered as a management technique (Morris et al., 2000). To try to reduce nutrient inputs into the catchments, economic incentives are given to significant aquatic polluters, such as farmers, to reduce their nutrient input into rivers (Morris et al., 2000). This incentive has been shown to help reduce high nutrient concentrations within eutrophic rivers (Greenhalgh and Sauer, 2003). There is currently a lack of knowledge on the links between nutrient status, hydrology and functioning of floodplain fens for successful fen restoration (van Diggelen et al., 2006), especially in relation to the radiative forcing of such environments.

2.3. Macronutrient cycling

Substrate nutrient status and biogeochemical cycling play an important role in the maintenance of peatlands, through the production of bioavailable nutrients for plant and microbial uptake, as well as the retention and accumulation of macronutrients (Mitsch and Gosselink, 2007). The biogeochemical processes that occur within peatlands also release GHGs and need to be understood to reduce the radiative forcings of floodplain fens.

2.3.1 Carbon and nitrogen cycles

The C and N cycles are two of the most important biogeochemical cycles within peatlands, limiting plant growth, altering microbial transformations and impacting on GHG efflux.

2.3.1.1 C cycle

The C cycle is fundamental to peatland formation and maintenance. CO_2 is taken up by vegetation from the atmosphere via photosynthesis (Figure 2) (Frolking et al., 2006). This total rate of CO_2 fixation is also known as GPP. Roulet (2007) estimated that northern peatlands take up 0.1 to 0.5 Pg CO_2 yr^{-1}, however, this may not be representative for lowland peatlands due to increased nutrient status and varying peat depths (section 2.3.4). A fraction of the C captured by photosynthesis is sequestered in accumulating peat (section 2.2.2.2) (Gorham, 1991, Frolking et al., 2006).

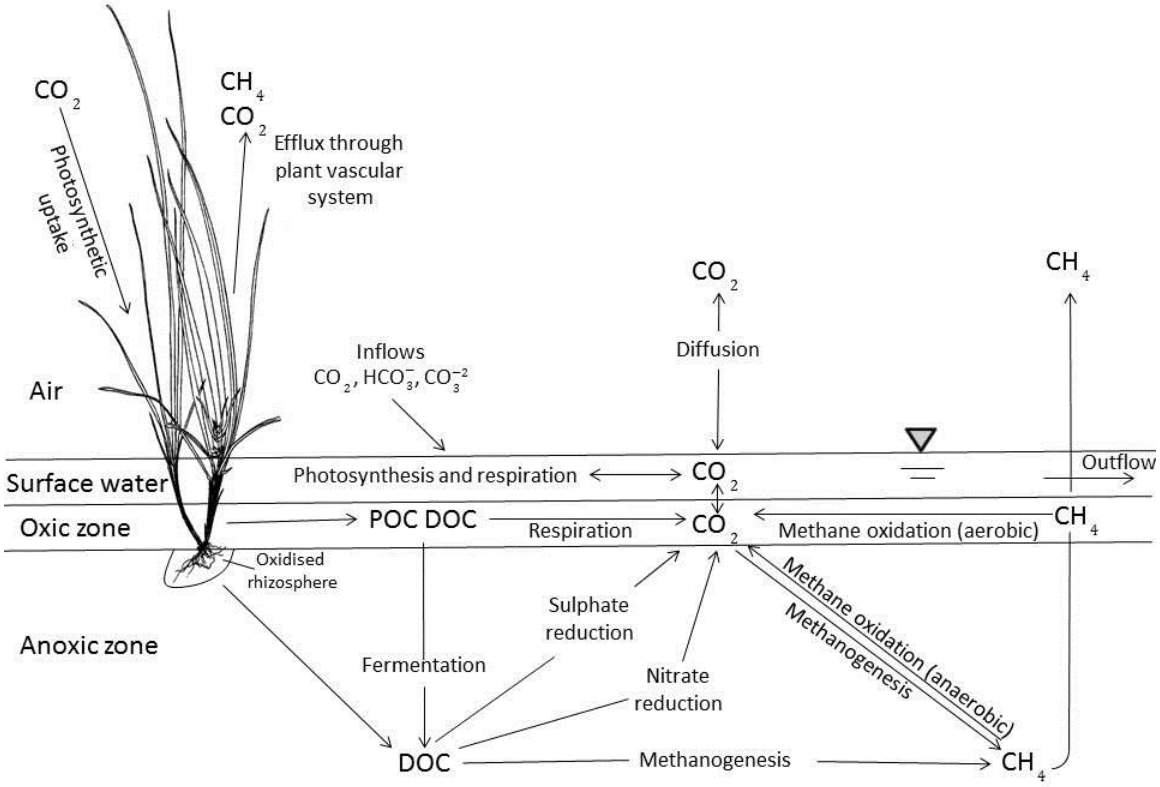


Figure 2 C cycle in peatlands. Adapted from Mitsch and Gosselink (2007, pg.187)

Once C is sequestered in peat, OM is decomposed aerobically and anaerobically (Figure 2). In oxic zones of peat, aerobic autotrophic and heterotrophic respiration converts OM into CO_2 (Eq. 1) (Frolking et al., 2006, Mitsch and Gosselink, 2007). The oxidation of glucose to CO_2 is done through a chain of reactions (glycolysis, oxidation of Pyruvate to Acetyl CoA, the Krebs Cycle and electron transport phosphorylation), which releases chemical energy (e^-) from the OM as no other form of energy (e.g. light or heat) is produced (Lambers and Ribas-Carbo, 2005). In glycolysis, glucose ($C_6H_{12}O_6$) is oxidised to pyruvate ($2CH_3COCOO^-$), which is then subsequently oxidised to Acetyl CoA, releasing 2 molecules of CO_2 per one molecule of pyruvate. The Acetyl CoA then undergoes oxidation through the Krebs cycle, releasing a further 4 molecules of CO_2. H_2O is then produced in electron transport phosphorylation, whereby electrons and H^+ move down an energy gradient to meet an ultimate electron acceptor (H_2O) or free electrons.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 12e^- + \text{energy} \qquad \text{Eq. 1}$$

Plants use autotrophic respiration to oxidise organic C into CO_2, whereas heterotrophic respiration is carried out by microbial populations (Frolking et al., 2006, Mitsch and

Gosselink, 2007). The combination of both heterotrophic and autotrophic respiration is also known as R_{eco}. Heterotrophic respiration occurs at a redox potential of between +250 mV and +600 mV, when O_2 is present as an electron acceptor. The production of CO_2 by aerobic respiration is a fairly energy efficient process (Clymo and Pearce, 1995). Once NO_3^-, Mn^{2+}, Fe^{2+} and SO_4^{2-} have been reduced, fermentation and methanogenesis can occur. This only occurs at a redox potential of below -250 mV. Many peatlands provide the habitats for methanogens (Smemo and Yavitt, 2011), the archaea that produce significant quantities of CH_4, which can be produced either during the fermentation process or by reducing CO_2 or low-molecular weight organic compounds. The combination of GPP and R_{eco} is often referred to as net ecosystem exchange (NEE) and is a measure of net CO_2 exchange within an ecosystem; showing if more CO_2 is emitted (positive flux) or sequestered (negative flux) at a given point in time (Chapin et al., 2006).

As there is no single functional group of microbes that can completely decompose complex polymers in peat, a number of successive transformations by microorganisms are needed for the fermentation process (Le Mer and Roger, 2001, Lai, 2009). Firstly, biological polymers are transformed into monomers such as glucides, fatty acids and amino acids by hydrolysis. This is undertaken by aerobic or anaerobic hydrolytic microfauna (Le Mer and Roger, 2001). Then, the monomeric compounds are transformed into intermediary compounds through acidogenesis, producing volatile fatty acids, organic acids, alcohols, H_2 and CO_2 by fermentative microflora that are obligate anaerobes (Le Mer and Roger, 2001). Then acetogenesis, the production of acetate from CO_2 and an electron source, occurs from the previous metabolites by syntrophic or homoacetogenic microflora.

Finally methanogenesis can take place using the simple compound produced in acetogenesis, such as acetate (Eq. 2) (Segers, 1998, Le Mer and Roger, 2001, Lai, 2009).

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad \text{Eq. 2}$$

Methanomicrobiales, CO_2 reducing microbes, also produce CH_4 through the reduction of CO_2 , and the use of H^+ as an electron donor (Eq. 3) (Cadillo-Quiroz et al., 2008, Lai, 2009).

$$CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O \qquad \text{Eq. 3}$$

The availability of reactants and electron donors control the pathway for CH_4 production, with environments high in CO_2 favouring *Methanomicrobiales*. The latter process, hydrogenotrophic methanogenesis, is generally the more dominant process in ombrotrophic bogs due to low pH values causing a fundamental disconnect between acetogenesis and acetoclastic methanogenesis (Duddleston et al., 2002, Yavitt and Seidman-Zager, 2006, Bridgham et al., 2013). This causes a build-up of acetate within ombrotrophic peatlands, resulting in a high CO_2:CH_4 production ratio. This ratio is much less within minerotrophic peatlands, of around 1-2 (Roulet, 2000), due to the dominance of acetogenic methanogenesis (Duddleston et al., 2002, Yavitt and Seidman-Zager, 2006, Bridgham et al., 2013).

Fen water levels have a very dramatic impact on CH_4 emissions, as methanogens are strict obligate anaerobes. With greater evapotranspiration rates and lower precipitation rates expected due to climate change, water tables in fens may well be altered. If oxic zones become greater and anoxic zones reduce in size, a consequent reduction of CH_4 production may be observed (Kettunen et al., 1999). Temperature and pH also control the rate of methane production, with optimum values being between 30 to 40 °C and around neutrality, respectively (Le Mer and Roger, 2001).

Emissions of CH_4 from floodplain fens are not only controlled by production rates, storage and transport rates (section 2.3.2), but also by CH_4 oxidation (Frenzel and Karofeld, 2000). CH_4 oxidation can occur either aerobically or anaerobically (section 2.3.4.3) through different processes. Aerobic CH_4 oxidation is undertaken by methanotrophs that are strictly aerobic bacteria (Modin et al., 2007), and occur where there is a steady supply of CH_4. CH_4 is one of the least reactive organic molecules and thus to overcome this activation energy cost, methanotrophs use molecular oxygen in the reaction (Eq. 4) (Ettwig et al., 2010).

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2 \qquad \text{Eq. 4}$$

Between 50 to 90% of CH_4 produced in the anaerobic zone may be oxidised to CO_2 in the oxidised zones, such as the rhizosphere and the oxic soil-water interface, before it reaches the atmosphere (Le Mer and Roger, 2001, Bodelier, 2011). Hence, aerobic methane oxidation is a significant source of CO_2 to the atmosphere for diffusive fluxes. Approximately 10 % of this oxidation process is associated with high affinity oxidation, which occurs at CH_4 concentrations close to the atmosphere, whilst the remaining activity is associated with low affinity oxidation that occurs at CH_4 concentrations higher than 40

ppm (Le Mer and Roger, 2001). Free-phase gaseous CH_4 released to the atmosphere by ebullition and plant-mediated transport bypass this oxidation. The main limitation to methanotrophic processes is the availability of oxygen and CH_4 (Le Mer and Roger, 2001, Hornibrook et al., 2009). CH_4 can be taken up from the atmosphere for the process at shallower depths if concentrations are not large enough.

2.3.1.2 N cycle

N is another macronutrient that is important in floodplain fen environments, as it controls plant and microbial population growth, as well as producing N_2O. NH_4^+ is the predominant form of N within peatlands, mineralised from OM during ammonification, a process heavily influenced by organic C mineralisation as the two are often bonded together in plant litter and soil OM (Mitsch and Gosselink, 2007, Reddy and DeLaune, 2008). NH_4^+ is either taken up by plants via their rooting systems or immobilised or transformed into other forms of N via nitrification and anammox by microbes (Mitsch and Gosselink, 2007). Generally, peatlands are N, P or N and P limited due to efficient microbial and plant uptake of N for growth (Wassen and Olde Venterink, 2006, Mitsch and Gosselink, 2007).

N enters the floodplain fen environment via three main pathways (Figure 3): N_2 fixation, atmospheric deposition and surface water inputs (Aerts, 1997a, Mitsch and Gosselink, 2007, Deyan and Changchun, 2010). N fixation converts atmospheric N_2 gas to organic N in organisms with the enzyme nitrogenase, such as algae and legumes (Mitsch and Gosselink, 2007). This process provides N in a bioavailable form for the fixing organisms to use. N is deposited on ecosystems either via wet or dry deposition and has become an important input in ecosystems within the past century due to increasing anthropic atmospheric pollution (Aerts, 1997a). Furthermore, N flows into floodplain fens via surface water and groundwater, which has also increased over the past century due to increased aquatic pollution from agriculture and industry (Aerts, 1997a, Aerts and de Caluwe, 1999, Deyan and Changchun, 2010). N enters the fen via surface water or groundwater either in a soluble or sediment-bound form, with the former being more bioavailable.

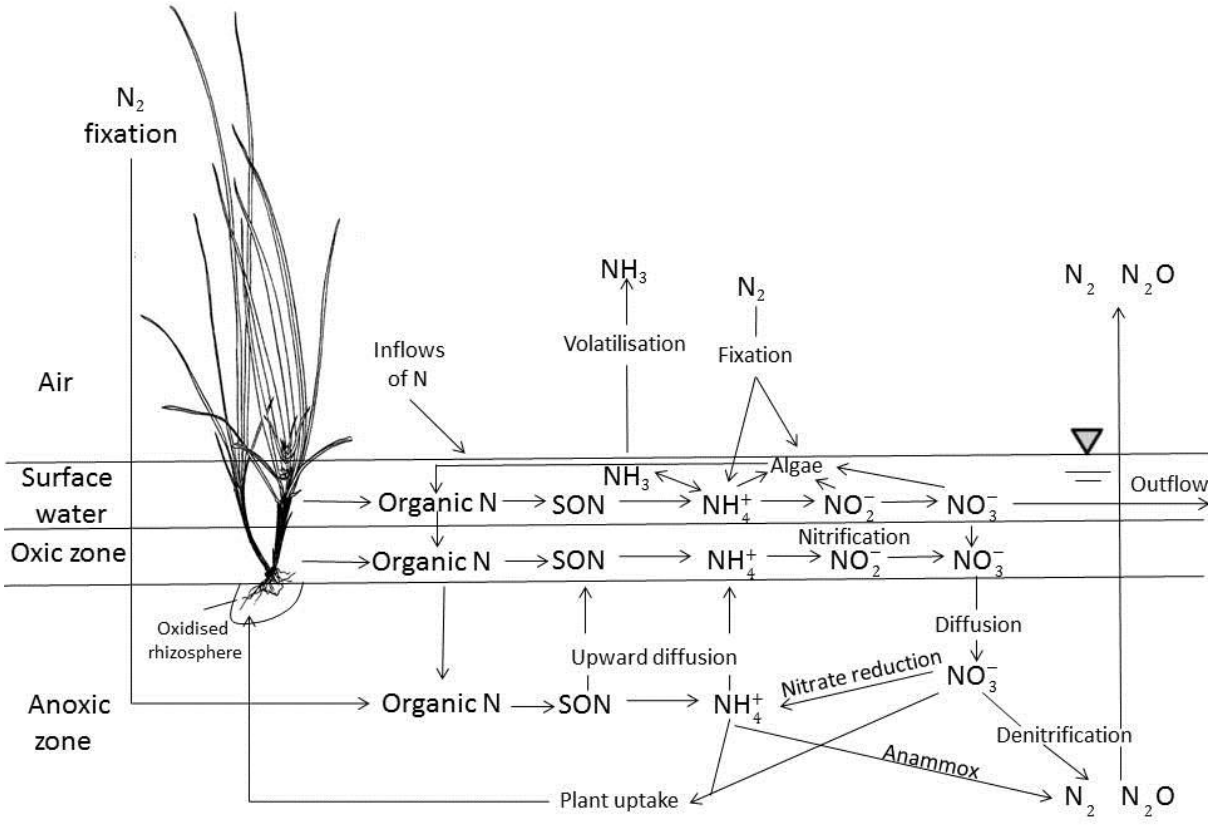


Figure 3 N cycle in peatlands. Adapted from Mitsch and Gosselink (2007, pg. 178).

Once N has entered the fen, organic N is mineralised, occurring both aerobically and anaerobically. Ammonification is both an aerobic and anaerobic process that is 2.5 times faster in aerobic environments than in anaerobic environments (Moore and Dalva, 1997, Frenzel and Karofeld, 2000), due to higher energy efficiency in oxic conditions. Ammonification is a process that transforms organic forms of N to NH_4^+ (Kuenen, 2008, Reddy and DeLaune, 2008). It is an oxidation process undertaken by general-purpose heterotrophs that use nitrogenous organic compounds as an energy source (Reddy and DeLaune, 2008). It is heavily influenced by the decomposition of organic C, as organic N is often bonded to organic C in plant litter and soil organic matter (Reddy and DeLaune, 2008). Once N is present in the NH_4^+ form, it can take a number of pathways (Mitsch and Gosselink, 2007). It can either be taken up by plants through their roots or used by microorganisms to immobilise the N or transform the N into other N species via anammox and nitrification (Figure 3) (Mitsch and Gosselink, 2007).

Nitrification, a purely aerobic process, is the oxidation of ammonium to nitrate and is a facultative process (Eq. 5) by ammonium oxidising bacteria and archaea (Andert et al., 2011).

$$NH_4^+ (\rightarrow N_2O) \rightarrow NO_2^- \rightarrow NO_3^- \quad \text{Eq. 5}$$

It is a process that is involved indirectly in the production of N_2O either by producing NO_3^-, which can then be denitrified to N_2O (via nitrification-denitrification), or by forming N_2O as a by-product during the oxidation of NH_4^+ to NO_3^- (Eq. 5) when sub-optimal oxygen concentrations for oxidation occurs (Bange, 2000, Machefert et al., 2002). The latter process is known as nitrifier denitrification, which is carried out by autotrophic nitrifiers, and can occur in low oxygen conditions with low organic C contents (Machefert et al., 2002, Kool et al., 2011). With NH_4^+ being the dominant input from fertilisers (Min et al., 2011), nitrification and nitrifier denitrification can prove to be significant sources of N_2O if the right conditions prevail.

For nitrification to take place, a ready supply of C is needed for an energy source, as well as NH_4^+ as a reactant. It has also been suggested by Tate and Salcedo (1988) that P may also control the rate of nitrification in some substrates. However, temperature, pH and organic matter quality are more important controls on nitrification (Tate and Salcedo, 1988). With growing concentrations of inorganic fertilisers being added to agricultural land, floodplain fens in agricultural catchments may receive increased concentrations of NH_4^+, which in turn drives nitrification processes and possibly increases N_2O emissions. N cycling in peatlands is very rapid due to NO_3^- being the next electron acceptor after oxygen (Figure 1), with free energy in the redox ladder (Smemo and Yavitt, 2011).

Anammox is the anaerobic oxidation of ammonium coupled with nitrite reduction (Eq. 6) (Kuenen, 2008, Zhu et al., 2010).

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \quad \text{Eq. 6}$$

This microbial transformation is a newly discovered pathway in the global N cycle that was initially discovered in wastewater treatment systems before being observed in natural environments, such as a peat bog (Kuenen, 2008). Currently no research has been published on anammox processes in floodplain fens, or in fenlands in general.

Once the redox potential is below +250 mV and oxygen is depleted and can no longer be used as an electron acceptor, one of the first reactions to occur in an anaerobic substrate is the reduction of NO_3^- to NO_2^-, and ultimately into NO, N_2O or N_2 (Bange, 2000, Mitsch and Gosselink, 2007). This process is also known as denitrification. For this transformation, anaerobic conditions and a ready supply of C is needed as an energy supply, as well as NO_3^- as a reactant. Denitrification will have a different end product depending upon the level of soil moisture, with N_2O being favoured by lower soil moisture, due to higher oxygen availability, and N_2 being favoured at the highest soil moisture as less oxygen is available (Machefert et al., 2002). The literature suggests that a soil moisture content of around 60 - 70 % by weight is the ideal condition for N_2O production and emission (Machefert et al., 2002). Availability of C and N, temperature and pH have also been shown to alter N_2O:N_2 production ratios (Weier et al., 1993, Smith, 1997, Lind et al., 2013), ranging between 0 to 549 depending on the conditions that prevail (Weier et al., 1993).

2.3.2 GHG storage and emission

Once CO_2 and N_2O have been produced, they are stored in the peat or emitted via molecular diffusion, or plant-mediated transport. After production, CH_4 can be emitted via molecular diffusion, plant-mediated transport or ebullition. Hydrology plays an extremely important role in the storage and control of GHG emissions. When GHGs are produced in the waterlogged peat, gases can be stored in an aqueous form or a gaseous form. The presence of each gas in either form is dictated by Henry's law, stating that the concentration of dissolved gas will be equivalent to the partial pressure of the gas, multiplied by its solubility (Strack et al., 2005). CH_4 is relatively insoluble (Table 1) and is generally found in a gaseous form as bubbles, whilst CO_2 and N_2O are relatively soluble (Table 1), thus are generally stored in aqueous form.

Table 1 CO_2, CH_4 and N_2O solubility in water at different temperatures and salinities.

Gas	Gas solubility in water (10^{-2} moles L^{-1} atm^{-1})				Reference
	Salinity: 0 ‰		Salinity: 36 ‰		
	0 °C	30 °C	0 °C	30 °C	
CO_2	7.758	2.983	6.689	2.561	Weiss (1974)
CH_4	0.36	0.18	0.28	0.15	Yamamoto et al. (1976)
N_2O	5.870	2.156	4.716	1.811	Weiss and Price (1980)

Due to CH_4's low solubility, CH_4 often forms free-phase gas bubbles. In order for free-phase gas bubbles to be formed, the partial pressure of all dissolved gases in solution must be greater than the hydrostatic pressure of the peat (Strack et al., 2005). As hydrostatic pressure increases linearly with depth, greater concentrations of dissolved CH_4 are needed for free-phase gas bubbles to form in deep peat layers than in shallower layers (Stamp, 2010). Temperature also plays a role in gas solubility (Table 1), with gases being more soluble at lower temperatures (Strack et al., 2005). Thus with the increase in peat temperature during the summer months, gas solubility will decrease and potentially lead to a net transfer of CH_4 from the dissolved phase to free-phase gas (Strack et al., 2005).

The presence of bubbles in the saturated zone has an impact on peat biogeochemistry: potentially altering trace gas exchange, porewater concentration gradients, O_2 diffusion rates and nutrient transport (Strack et al., 2005). Localised gas diffusion gradients develop and affect reactant delivery by displacing porewater (Strack et al., 2005). Additionally, local flow paths can be affected by the blockage of pores with small diameters, reducing the ability of larger bubbles to pass through and hindering bubbles that may be moving through the peat profile (Strack et al., 2005). The accumulation of bubbles, as well as the presence of bubbles, can alter the buoyancy of floating peat.

Ebullition (Figure 4) is the means of gas transport to the atmosphere via bubbles. After bubble formation, the bubbles are transported to the atmosphere, bypassing the oxidising effects of the unsaturated peat layer and rhizosphere (Chanton, 2005), making this transport mechanism extremely important due to the potential for significant CH_4 emission. Bubble release can be caused by a number of triggers, such as pressure differences, wind events, falling hydrostatic pressure or changes in atmospheric pressure (Strack et al., 2005, Kellner et al., 2006, Coulthard et al., 2009). CH_4 is the main gas that is transported via this mechanism, as it is only sparingly soluble in water (Chanton, 2005). In a study by Glaser et al. (2004) in a fen in Minnesota, USA, it was found that rates of ebullition release can be very large, with number of events emitting > 40 g CH_4 m^{-2} within hours. Other studies, such as Stamp et al. (2013), Strack et al. (2005) and Coulthard et al. (2009), have shown ebullition to be highly spatially and temporally variable with fluxes between 0 and 100 mg CH_4 m^{-2} h^{-1}. Stamp et al. (2013) showed ebullition hotspots within a Welsh patterned raised bog, emitting significantly greater amounts of CH_4 than the surrounding areas sampled.

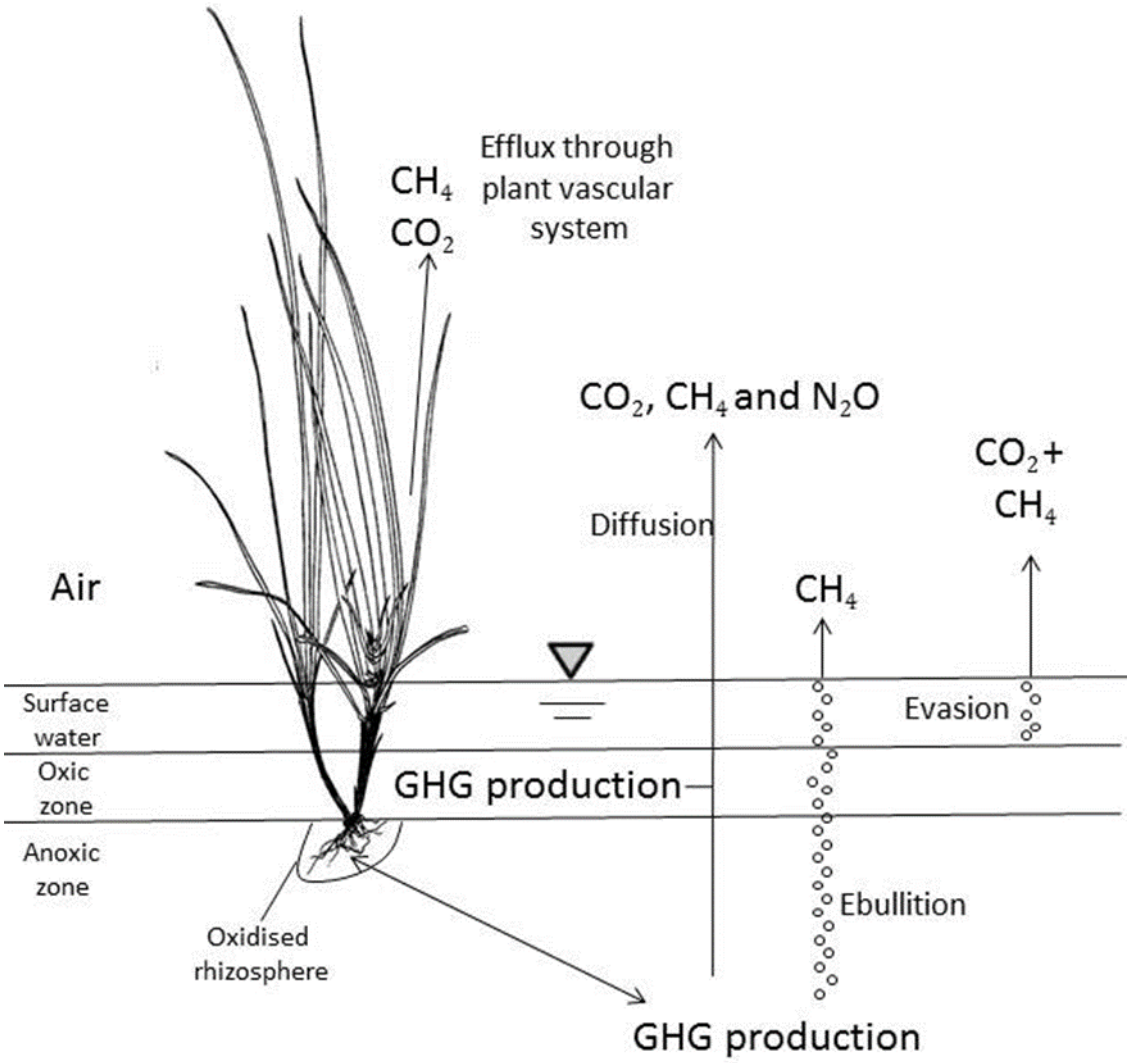


Figure 4 Four mechanisms of gas transport from peatlands: diffusion, ebullition, evasion and efflux through plant vascular system.

Ebullition is episodic in nature due to its driving processes and can therefore be very difficult to quantify. A number of studies have developed a funnel trap method to quantify ebullition fluxes, such as Strack et al. (2005) and Stamp et al. (2013), for a poor fen and an upland bog, respectively. Funnel traps are constructed from inverted laboratory funnels that have been adapted to have a cylinder with a specific volume at the top, which the gas bubbles collect in over time. The funnels are inserted into a hole cut for the funnel to a specific depth upside down (Strack et al., 2005). A bung with a sample tube through it is inserted into the funnel at the top of the cylinder and the funnels are filled with water from the peatland, as not to change the porewater chemistry (Strack et al., 2005). Gas emitted is monitored by measuring the volume of gas within the water

filled cylinder (Strack et al., 2005). Relatively few studies have quantified ebullition fluxes and more research needs to be done to better understand the process.

Molecular diffusion (Figure 4), occurs when there is a concentration gradient, with gas movement from higher concentration to lower. Diffusion rates are regulated by concentration, diffusion coefficient and substrate porosity (Chanton, 2005). Molecular diffusion follows Fick's first law:

$$J = \emptyset D dC/dz \qquad \text{Eq. 7}$$

where J is the diffusive flux (example units, mol cm^{-2} h^{-1}), D is the diffusion coefficient (cm^2 h^{-1}), $\emptyset$ is the porosity and dC/dz is the concentration gradient (C; mol cm^{-3}), as a function of depth or distance (z; cm) (Chanton, 2005). Porewater GHG concentrations in deeper layers of the peat substrate are generally higher than the atmosphere, driving the diffusive flux from the fen to the atmosphere. Currently, the importance of diffusion as a flux is not known in comparison to the other two mechanisms, ebullition and plant-mediated transport, as diffusive fluxes and steady ebullition (the release of free phase gas bubbles in a steady state) are difficult to separate when interpreting flux data (Strack et al., 2005, Strack and Waddington, 2008).

Plants also play an extremely important role in facilitating gas transfer of CO_2 and CH_4 to the atmosphere. Aerenchyma in a number of wetland plants act as a conduit for CO_2 and CH_4 (Chanton, 2005, Bodelier, 2011). These plants have developed systems to transport oxygen to their roots and rhizomes to support respiration and protect them from phytotoxins (Koncalova, 1990). The process can occur either passively or actively, depending on plant species. Passive transport of CO_2 and CH_4 occurs with the passage of gas through the aerenchyma due to a concentration gradient and occurs in sedge and rush species such as *Carex spp.* and *Juncus spp.* (Schäfer et al., 2012, Noyce et al., 2014). Noyce et al. (2014) found that *C. rostrata* had emission between 6 and 33 % greater than in cut plots, with fluxes ranging between 0.28 and 21 mg CH_4 m^{-2} h^{-1} in non-clipped plots. Schäfer et al. (2012) observed negligible CH_4 emissions in three Danish grasslands on peat, apart from in one site where *J. effusus* was present, emitting up to 3.3 mg CH_4 m^{-2} h^{-1}. Active transport occurs with the convective through-flow of gases, driven by a pressure difference, with gases passing from areas of high pressure to low pressure and occurs in reed and grass species, such as *P. australis* (Armstrong et al., 1992, Brix et al., 1996, Chanton, 2005). This pressure differentiation can be caused by

either thermal transpiration or from humidity differential across a leaf boundary (Chanton, 2005). However, this only generally occurs during daylight, as at night there is no pressure gradient within the plant to drive the convection and thus molecular diffusion is a more dominant transport mechanism (Chanton, 2005). Van Der Nat and Middelburg (1998) found that *P. australis* emitted significantly more CH_4 (20 to 80 mg CH_4 m^{-2} h^{-1}) than *Scirpus lacustris* (17 to 30 mg CH_4 m^{-2} h^{-1}) in a peat mesocosm experiment. This is also corroborated in Koch et al. (2014), where CH_4 emission was greater in pure stands of *P. australis*, with fluxes ranging between -5.1 to 61 mg CH_4 m^{-2} h^{-1}.

Chanton (2005) reported a difference in CH_4 emission between vegetated lowland marshes and adjacent non-vegetated areas. Fluxes were generally 10 times greater in the vegetated areas than in the non-vegetated areas, illustrating the importance of this transport mechanism for CH_4. Furthermore, CH_4 partial pressures within the peat where the plants were rooted were affected by ventilation, causing porewater concentrations to be approximately 50% lower than in non-vegetated areas and in turn it reduced the CH_4 concentration gradient out of the soil and decreased the diffusive flux (Chanton, 2005).

Finally, in peatland areas with surface water, such as ditches and hollows, evasion occurs. This is the vertical degassing of peatland surface waters that transports CH_4 and CO_2 from a supersaturated water body to the atmosphere (Billett and Moore, 2008). Evasion is driven by a pressure difference that occurs at the air-water interface, allowing for atmospheric exchange (Hope et al., 2004, Billett and Moore, 2008). Schrier-Uijl et al. (2010a) and Schrier-Uijl et al. (2010b) reported significant evasion rates from drainage ditches in Dutch floodplain fens. CO_2 evasion rates ranged from 70 to 199 mg CO_2 m^{-2} h^{-1} (Schrier-Uijl et al., 2010a), whilst CH_4 rates were significantly greater, ranging from 1.2 to 366 mg CH_4 m^{-2} h^{-1} (Schrier-Uijl et al., 2010b). Schrier-Uijl et al. (2010b) hypothesised that some of the higher evasion rates may be attributed to ebullition and not evasion, although the latter process was not quantified. Relatively few measurements have been made of evasion rates in UK peatlands, and this could be a large source of C from floodplain fens with ditch networks.

A number of different methods for quantifying diffusive and plant-mediated fluxes exist, including micrometeorological and chamber-based methods. Eddy covariance is the preferred means of micrometeorological GHG quantification, which relies on fast response anemometers and gas sensors to measure vertical gas flux (Denmead, 2008).

This method does have caveats, discussed in section 4.2. Gas fluxes are calculated using Eq. 8 and are frequently measured at frequencies of 10 Hz.

$$F_g = w \cdot \rho_g \quad \text{Eq. 8}$$

Where F_g is the gas flux (example units, µmol CH_4 m^{-2} s^{-1}), w is the vertical wind speed (m s^{-1}) and ρ_g is the gas concentration (µmol CH_4 m^{-3}). After data quality control and assessment and any necessary corrections and gap filling using techniques outlined in Moffat et al. (2007a) and Gomez‐Casanovas et al. (2013), data are often block averaged to half hourly covariances and summed over the year (Rinne et al., 2007, Denmead, 2008). Chamber techniques are the most commonly used technique due to simplicity and flexibility (section 4.2). A number of different chamber methods exist (see section 4.2 for a review): however, they are all based on a similar principle of measuring the concentration within an enclosed area, taking temperature and pressure differences into account. In closed chambers, the increase in gas concentration is used to calculate a flux either using linear or non-linear regression techniques (Pumpanen et al., 2004, Denmead, 2008, Forbrich et al., 2010). Generally, linear regressions are used to calculate GHG fluxes from closed chambers as it is assumed that the concentration build up in the chamber should be linear when the enclosure time is kept relatively short (Forbrich et al., 2010). It is also assumed that spatial variability in fluxes is much larger than the effect of incorrectly applying a linear regression (Forbrich et al., 2010). Non-linear methods have traditionally been refrained from being used due low temporal resolution needing very pronounced non-linearity for a significant detection and the error associated with fitting a poor non-linear regression (Forbrich et al., 2010). Linear and non-linear regression modelling techniques are used to infill between sampling points due to the non-continuous nature of chamber measurements, using environmental data recorded over frequent intervals to calculate fluxes at an hourly interval that can be summed to get an annual flux.

GPP, R_{eco}, CH_4 and N_2O fluxes vary seasonally due to environmental controls on photosynthesis, respiration, fermentation, methanogenesis and denitrification (section 2.3.3). Many studies report monthly or seasonal fluxes to show temporal variation in fluxes and to help discuss trends in data (e.g. Koebsch et al. (2013a), Koebsch et al. (2013b) and Audet et al. (2013a)). Annual fluxes, calculated either from eddy covariance data or from infill modelling for chamber measurements, are more frequently used to compare GPP, R_{eco}, CH_4 and N_2O fluxes between sites and between years. Additionally, CO_2, CH_4 and N_2O fluxes vary between different types of peatland. Generally fluxes tend to be greater in minerotrophic fens than ombrotrophic bogs (Table 2) due to the higher

nutrient inputs from groundwater and surface water (Drewer et al., 2010). In fens, taller vegetation, such as graminoids, and a greater aboveground biomass enable greater GPP than in bogs (cf. Wilson et al. (2007a) and Laine et al. (2007a)), where mosses and small sedges dominate. Greater GPP is countered by higher R_{eco} and CH_4 emission in fens than in bogs (Table 2) due to a great number of reactants for heterotrophic respiration and methanogenesis from hydrological inputs. Differences in N_2O emission between fens and bogs is generally very small. Fluxes greatly depend on N inputs into the system. The greater range in N_2O emission observed in Audet et al. (2013a) than many other peatland studies was attributed to the high N inputs into the system both from ground- and surface water and N availability due to OM mineralisation.

2.3.3 Controls on GPP, R_{eco} and CH_4 emission

Currently, no *in situ* study has tried to calculate the relative importance of biotic and abiotic controls on GPP, R_{eco} and CH_4 emission in floodplain fens. A number of studies have established if specific environmental parameters have a controlling influence using regression models for each respective environmental parameter and a gas flux (Riutta et al., 2007b, Audet et al., 2013a, Koebsch et al., 2013a, Koebsch et al., 2013b, Koch et al., 2014), which are discussed in the section below. It is important to establish the relative importance of environmental parameters to help inform current and future management practice.

2.3.3.1 Temperature

Temperature has been shown to have a significant effect on GPP, R_{eco} and CH_4 emission, causing large seasonal variations in fluxes (Audet et al., 2013a, Kandel et al., 2013b, Koebsch et al., 2013a, Koebsch et al., 2013b). Seasonal variations have been linked with changes in surface peat temperature, with this area of peat being affected the most by alterations in air temperature, due to the high correlation between soil and air temperatures, and having the highest peat temperatures (Coulthard et al., 2009).

Table 2 NEE, R_{eco}, CH_4 and N_2O fluxes reported in the literature (positive fluxes represent emission and negative indicate uptake).

Study	NEE (mg CO_2 m^{-2} h^{-1})	R_{eco} (mg CO_2 m^{-2} h^{-1})	CH_4 (mg CH_4 m^{-2} h^{-1})	N_2O (mg N_2O m^{-2} h^{-1})	Peatland type
Wilson et al. (2007b)	0 - 3500	0 - 2600			Rewetted floodplain fen
Koebsch et al. (2013a)	0 - 1069	0 - 1985			Floodplain fen
Hendriks et al. (2007)	-4764 - 733	0 - 3664	0 - 65		Floodplain peat meadow
Audet et al. (2013a)		0 - 1000	0 - 36	0 – 5.1	Floodplain fens
Pelletier et al. (2007)			0 - 341		Rich fen
Drewer et al. (2010)	-0.63 - -6		-0.15 – 24	0 – 0.02	Rich fen
	-14 - 21		0 – 0.63	0 – 0.01	Raised bog
Alm et al. (1999)	0 – 170		0 – 2.1		Rich fen
	2 - 100		0 – 0.05		Blanket bog
Martikainen et al. (1995a)	25 – 420		0 – 23		Fen
	25 - 375		0 – 2.3		Forested bog
Yamulki et al. (2012)		0 – 0.88	0 – 8.2	0 – 0.05	Forested raised bog
Laine et al. (2007b)			0.1 – 2.2		Lowland blanket bog
McNamara et al. (2008)		174 - 650	0.13 – 2.2		Upland blanket bog

Air temperature has been shown to increase photosynthetic uptake of C (Berry and Bjorkman, 1980), increasing plant growth rate, biomass and subsequently litter production and root exudate release. This increase in biomass, litter and root exudate release will have a subsequent impact on R_{eco} and CH_4 emission due to the supply of substrates (section 2.3.4.2). Additionally, the surface peat layer is the most important layer for methanogenesis and heterotrophic respiration due to the greater availability of labile C from litter and root exudates. Alterations to near-surface peat temperatures have been shown to change methanogenesis and heterotrophic respiration in temperate peatlands (Huth et al., 2012, Audet et al., 2013a, Kandel et al., 2013b) due to increases in microbial activity and biomass associated with temperature increases (Andersen et al., 2013).

Alterations in peat temperatures also affect gas solubility, with increasing temperatures reducing gas solubility within water (Weiss, 1974, Yamamoto et al., 1976, Weiss and Price, 1980), resulting in greater net transfer from aqueous to gaseous phase and subsequently larger diffusion/evasion rates (Strack et al., 2005). Increasing temperatures can also enhance ebullition by augmenting bubble size, causing increased buoyancy (Ideal Gas Law) and transfer to the atmosphere (Strack et al., 2005, Stamp, 2010). The ideal gas law defines the relationship in bubble expansion/contraction in response to temperature and pressure alterations. Owing to these interacting factors, GPP, R_{eco} and CH_4 fluxes might be expected to be greatest in summer and smallest in winter. Some authors have assumed or shown winter time fluxes to be negligible (Panikov and Dedysh, 2000, Huth et al., 2012) due to low temperatures. However, significant fluxes have been observed during winter in temperate fens despite extremely cold temperatures (Melloh and Crill, 1996, Huth et al., 2012).

2.3.3.2 Water level

In addition to temperature, water level has also been cited as a significant controlling factor on GPP, R_{eco} and CH_4 emission (Syed et al., 2006, Lindroth et al., 2007, Riutta et al., 2007b, Audet et al., 2013a, Koebsch et al., 2013a, Koebsch et al., 2013b). Water levels control the proportion of aerobic/anaerobic peat substrate due to water reducing oxygen diffusion by an estimated 10,000 times (Mitsch and Gosselink, 2007). CO_2 production occurs both aerobically via heterotrophic respiration and anaerobically via respiration and fermentation (section 2.3.1.1) (Frolking et al., 2006). Aerobic heterotrophic respiration is the more efficient process, with aerobic:anaerobic CO_2 production ratios varying within the peatland literature between 1.8:1 and 9.3:1 (Moore

and Dalva, 1993, Aerts and Ludwig, 1997, Blodau and Moore, 2003, Glatzel et al., 2004). In addition to controlling CO_2 production rates, water levels also affect CH_4 emission by controlling rates of methanogenesis and methanotrophy (Segers, 1998). Methanogens are strict obligate anaerobes, only functioning in the horizon of peat under anaerobic conditions, whilst methanotrophs are strict aerobes (Segers, 1998, Modin et al., 2007). A lowering of the water table may result in methanogens being inhibited by O_2, greater rates of methanotrophy and an increase in competition by aerobic microorganisms for C compounds used in methanogenesis (Segers, 1998).

Alterations to a peatlands water level can also affect transport to the atmosphere via plants and evasion. As water levels decrease, the rhizosphere will oxidise and aerobic heterotrophic respiration will become the dominant CO_2 production pathway and potentially greater rates of CO_2 emission may occur via plant-mediated transport than under anaerobic conditions. Methanogenesis will, however, be inhibited, reducing CH_4 emission through vascular plant's aerenchyma.

Water level also impacts upon GPP by putting stress on plants when water levels are high for sustained periods at the beginning of the growing season or below the rooting systems of plants. Koebsch et al. (2013a) observed a reduction of 46 % in GPP in a *P. australis* floodplain fen after an inundation event increasing the water level 25 cm above the average level of the preceding months. In contrast, Hatala et al. (2012) and Waddington et al. (2010) did not observe a decrease in GPP with inundation of a temperate fen and a boreal bog, respectively. For non-adapted plant species, flooding events can induce O_2 deprivation up to anoxia, inducing stomatal closure, and decreased metabolic activity (Koebsch et al., 2013a). For low water levels or drought conditions, negative effects such as an earlier senescence (i.e. a shorter growing season), less healthy and productive vascular plants, and a reduction in GPP have been observed (Sonnentag et al., 2010, Sulman et al., 2010). Sonnentag et al. (2010) observed a significant reduction in GPP in a boreal minerotrophic fen during a period of drought due to a reduction in aboveground biomass and an early onset of senescence. Muhr et al. (2011), however, did not observe a reduction in GPP with a decrease in water level by approximately 20 cm in a controlled water level manipulation experiment. The lack of effect may be due to the timing of the experiment, as Muhr et al. (2011) reduced the water level in July, mid-growing season for many plants. By this time, the majority of plants would be well-established and the stress incurred from the lowing of the water table is less than at the beginning of the growing season when plant species are more

vulnerable to drought-induced stresses. With seasonal water-level alterations dependent on precipitation, groundwater and surface water inputs, evapotranspiration and plant uptake of water, it might be expected that water levels are lowest during the summer months and higher during winter months, due to higher inputs and smaller loss of water in the winter months.

2.3.3.3 Barometric pressure (CH_4)

Changes in barometric pressure have been attributed to inducing the episodic release of CH_4 via ebullition (Tokida et al., 2005, Tokida et al., 2007, Yu et al., 2014). A drop in barometric pressure and an increase in temperature can increase bubble volume and buoyancy in existing free-phase gas bubbles (Ideal Gas Law) and enhance new bubble formation or growth of existing bubbles as gases come out of solution (Henry's law; Strack et al. (2005), Stamp (2010), Yu et al. (2014)), causing greater bubble release. Not all ebullition studies have, however, observed the effect of falling barometric pressure on ebullition events, including Rosenberry et al. (2003), Kellner et al. (2006) and Strack et al. (2005). Peat type and structure may also have a large control on ebullition, entrapping gas bubbles. A peat matrix with large debris in, such as partially decomposed woody debris, may allow for the accumulation of larger gas bubbles below the debris before being emitted than in a more homogenous matrix of homogenous peat with large pore spaces (Glaser et al., 2004, Coulthard et al., 2009, Comas et al., 2014). Glaser et al. (2004) observed a confining layer of woody debris at depths between 2 – 3 m in a boreal bog, which impeded bubbles and caused very large ebullition events (e.g. 35 g CH_4 m^{-2} per event) to occur when triggered. Peat structure affects pore sizes in between the peat particles in which entrapped gas can be present (Strack et al., 2005, Comas et al., 2014), with larger pore sizes allowing greater accumulation of gas within a bubble. However, no empirical study has quantified the relationship between peat structure and ebullition rates.

2.3.3.4 Vegetation and PAR

One of the primary controls on C fluxes within peatlands is a source of high quality organic matter from above- and belowground plant biomass and root exudates (Matson and Harriss, 1995). GPP is highly dependent on green aboveground biomass and incoming solar radiation in the form of PAR for CO_2 assimilation. Greater green photosynthesising area and photosynthetic photon flux density (PPFD) result in greater rates of GPP (Laine et al., 2007a, Riutta et al., 2007b). A number of studies have also observed positive correlations of CH_4 emission and R_{eco} with GPP, attributed to the

release of labile root exudates and stimulation of methanogenesis and heterotrophic respiration/fermentation (Whiting and Chanton, 1993, Bubier et al., 1998). An increase in aboveground biomass has the potential to increase root exudate release and provide greater quantities of labile C for methanogenesis and R_{eco}. Alterations in aboveground biomass also have the potential to change the extent of oxidation around the rhizosphere. A greater abundance of plant species with aerenchyma may increase the oxidised rhizosphere and potentially increase R_{eco} and denitrification rates, whilst reducing methanogenesis due to the poisoning of methanogens with O_2 (Segers, 1998).

Vegetation not only has an impact on the production and sequestration of CO_2 and CH_4, it also affects the transportation of the two gases. Rates of gas transport through the two main types of gas transporting plants (section 2.3.2) will change with alterations in aboveground biomass and species composition and abundance. Passive CO_2 and CH_4 fluxes from plant species such as *Carex spp.* and *Juncus spp.* would increase with an increase in plant abundance and number of leaves, as there would be a greater number of aerenchyma for root to atmosphere gas transfer (Chanton, 2005). An increase in aboveground biomass does not, however, necessarily result in greater active gas transport from plants, such as *P. australis*, as active efflux is driven by pressure differences caused by wind passing over dead culms (Armstrong et al., 1992, Brix et al., 1996, Chanton, 2005). Therefore, active plant-mediated gas efflux is dependent on both living and dead culms to create the cyclical gas movement.

2.3.3.5 Relative humidity and wind speed

Relative humidity and wind speed have been shown in peatland environments to alter gas transport mechanisms. Relative humidity has been shown in the past to affect rates of GPP by altering stomatal conductance, reducing conductance with an increase in relative humidity (Aphalo and Jarvis, 1991). More recently, water vapour saturation deficit, the difference between water vapour concentrations inside stomata and ambient air, has been shown to better describe stomatal responses to humidity rather than relative humidity directly (Aphalo and Jarvis, 1991, Monteith, 1995). However, there is some debate to what extent relative humidity indirectly drives stomatal conductance in peatlands, with Sonnentag et al. (2010) and Otieno et al. (2009) observing no effect of relative humidity on stomatal conductance.

Wind speed affects both active plant-mediated gas transport (section 2.3.3.4) and evasion rates from open water bodies (Armstrong et al., 1992, Matthews et al., 2003). Wind speed has been shown to have an impact on CH_4 emission in a boreal fen, with variation in fluxes being partially explained by wind speed, along with peat temperature, for speeds < 1.5 m s^{-1}, yet speeds > 1.5 m s^{-1} had no impact (Suyker et al., 1996). Armstrong et al. (1992) have shown that wind velocity has an impact on convective through flow of gases in aerenchymatous plants. Pressure differences develop between the top of the vegetation and the rhizosphere, driving the flow of oxygen into the rhizosphere and CH_4 out into the atmosphere (Armstrong et al., 1992, Brix et al., 1996). Culms with larger sectional areas emit more CH_4 as emission is proportional to sectional area (Armstrong et al., 1992). Wind speed alters evasion rates from water bodies by disturbing the air-water boundary layer, which induces a net loss of CO_2, CH_4 and N_2O under supersaturated conditions (Matthews et al., 2003). Billett and Moore (2008) found CO_2 evasion to be 1.5 times greater in running water bodies than in static water bodies in a boreal oligotrophic bog and attributed the differences to turbulence in the air-water boundary inducing evasion. Wind can also induce such turbulence in the air-water boundary, although no study to date has shown this relationship.

2.3.3.6 pH

pH has been shown to be a very important controlling factor on methanogenesis, as methanogens are known to be neutrophillic (Koebsch et al., 2013b). However, a number of studies have reported different relationships between pH and methanogenesis (Segers, 1998, Whalen, 2005). Additionally, pH is not the most important factor in controlling methanogenesis and emission, with other factors such a water level and peat temperature playing a larger role in controlling fluxes (Bubier, 1995, Segers, 1998, Koebsch et al., 2013b). pH has not generally been shown to be a controlling factor on R_{eco} *in situ* in peatlands, as autotrophs are generally specific to their environment. However, CO_2 production usually increases with pH when less than pH 7 and decreases when greater than pH 7 (Yiqi and Zhou, 2010). As for CH_4 emissions, peat temperature and water level play a more important role in R_{eco} than pH. pH has not been shown to be a direct controlling factor on GPP in lowland fens previously. pH does, however, influence plant species composition. Mosses are more abundant in acidic conditions, whilst taller vascular plants tend to favour more neutral conditions (Grime et al., 2007).

2.3.4 Effects of nutrients on storage, production and emission of GHGs

Relatively few studies have been undertaken on the relative importance of N and P on GPP, R_{eco}, CH_4 and N_2O emissions in peatlands. N and P contents/concentrations influence ecosystem functioning within peatlands, impacting on a number of different processes, such as plant growth (section 2.3.4.1), microbial processes and rates (section 2.3.4.2 and 2.3.4.3), effecting C and N exchange via GPP, respiration, fermentation, methanogenesis, methanotrophy and denitrification. A small number of studies have been undertaken *ex situ* to try to elucidate alterations to C and N cycling (Amador and Jones, 1993, Aerts and Toet, 1997, Watson and Nedwell, 1998, Aerts and de Caluwe, 1999). A greater number of studies have been undertaken in mineral soils. The findings from both *ex situ* peat and mineral soils studies are discussed in the following sub-sections.

2.3.4.1 N/P limitation in plants

N and P are two growth-limiting nutrients for floodplain fens. Currently, many peatland plants are N and P limited due to the environmental conditions that prevail, with high water tables reducing mineralisation of OM, resulting in the supply of bioavailable N and P falling below the demand by plants and microbes (Wassen and Olde Venterink, 2006, Mitsch and Gosselink, 2007). The N and P limitation on plants can result in reduced plant growth but greater species diversity (Wassen and Olde Venterink, 2006, Koelbener et al., 2010). If nutrients are scarce, plants often have a large belowground biomass to ensure enough resources are obtained (Rydin and Jeglum, 2013). It has been reported that increases in peat N and P contents due to anthropic inputs increase aboveground and belowground biomass (Nykanen et al., 2003, Zhang et al., 2007), as well as increasing C sequestration due to the increased biomass.

Nutrient enrichment, which is occurring all over the world from anthropic activities can lead to changes in species composition and a lack of diversity (Wassen and Olde Venterink, 2006, Koelbener et al., 2010). Greater N content in plant leaves via nutrient enrichment has been shown to lead to greater rates of photosynthesis and higher C sequestration rates (Liu and Greaver, 2009). The increased foliar nutrient contents can alter decomposition rates (Aerts, 1997b, Hoorens et al., 2003, Knorr et al., 2005) due to the increased number of reactants within the foliar biomass. If water levels are high, this can result in C storage via peat accumulation. Alterations to surface litter can change microenvironmental variables which control plant community composition (Weltzin et al., 2005), which could potentially alter litter quality. P limitation affects N fixation in legumes

and cyanobacteria (Kranabetter et al., 2005). Both greater N and P foliar contents should allow for greater uptake of C and N from the atmosphere and subsequent long-term storage, if prevailing conditions are conducive to peat accumulation (section 2.2.2.2).

Increased N and P concentrations have also been found to alter R_{eco}, CH_4 and N_2O fluxes due to alterations to vegetation and microbes (Liu and Greaver, 2009). Fluxes from vegetation are modified with the increase in abundance and biomass, possibly leading to greater CH_4 emissions (Whiting et al., 1991, Whiting and Chanton, 1993, Bellisario et al., 1999, Ding et al., 2003). Furthermore, an increase in the oxidised rhizosphere due to greater plant abundance (Blom, 1999) can potentially increase microbial fluxes of CO_2 and N_2O due to the aerobic conditions, allowing for increased heterotrophic respiration and greater nitrification and nitrifier denitrification.

2.3.4.2 N/P limitation of microbes

Peat and porewater N and P contents/concentrations greatly affect microbial populations, controlling mineralisation and GHG production processes. Increases in nutrient contents allow for microbial populations to grow, as well as increasing microbial decomposition of OM, as the nutrients act as reactants for the processes (Ouyang et al., 2008). Additionally, roots that have higher N and P contents have been found to decompose more quickly than those with lower concentrations (Tate and Salcedo, 1988, Liu and Greaver, 2009), adding to labile C, N and P sources. Mineralisation has been found to augment with increased N and P concentrations due to microbial population growth. N and P are often limiting in mineralisation processes (Basiliko et al., 2007). The relationship between C, N and P contents on mineralisation rates is not straightforward. With greater inputs of anthropogenic N and P into floodplain fens, either by atmospheric or fluvial deposition, mineralisation and immobilisation processes may be affected.

N and P additions have been shown to alter heterotrophic respiration. Both NH_4^+ and NO_3^- have been shown to increase respiration by stimulating the microbes and providing them with reactants for mineralisation (Min et al., 2011). Amador and Jones (1993) found that high concentration NH_4^+ applications to peat stimulated respiration and CO_2 emission when total P contents were high. NH_4^+ has been shown to stimulate respiration more than NO_3^- due to lower energy costs from a better biological preference and ionic charge (Min et al., 2011). Furthermore, according to stoichiometric decomposition theory, increased N availability allows for energy to be saved by microbes as they no longer

acquire N (Min et al., 2011). PO_4^{3-} has also been shown to stimulate respiration, providing reactants for the process and allowing biomass to proliferate (Amador and Jones, 1993). Amador and Jones (1993) found that in P-limited peat, the application of low concentrations of P (below 10mM PO_4^{3-}) increased soil respiration.

However, both N and P have also been shown to inhibit respiration. Amador and Jones (1993) found that high concentrations of PO_4^{3-} (100mM PO_4^{3-}) inhibited respiration in peat by altering the C:P contents in the substrate and increasing C immobilisation rates. NH_4^+ additions decrease the substrate pH, aggravating microbes and limiting their functioning (Aerts and de Caluwe, 1999, Ouyang et al., 2008). NH_4^+ additions have also been shown to reduce methanogenesis, aggravating the microbes with the reduction in pH, as they work most efficiently in neutral or under slightly alkaline conditions (Amador and Jones, 1993, Le Mer and Roger, 2001). NO_2^- and NO_3^- are non-specific methanogenic inhibitors (Smemo and Yavitt, 2011). There were two theories that were postulated as to why NO_2^- and NO_3^- inhibit methanogenesis, including the drop in redox potential and the competition for reactants between methanogens and denitrifiers. They were both found not to be the cause, as the intermediates of denitrification (NO_2^-, NO_3^- and N_2O) were found to be toxic to methanogenic archaea (Roy and Conrad, 1999, Smemo and Yavitt, 2011).

PO_4^{3-} has been shown to stimulate methanogens and methanogenesis (Aerts and Toet, 1997, Aerts and de Caluwe, 1999), as microbes are often P limited in peatlands (Basiliko et al., 2007). Despite the higher C, N and P contents in fen peat, mineralisation rates of N and P have been found to be higher in oligotrophic bogs (Verhoeven et al., 1990, Bridgham et al., 1998). This may be due to higher total P contents in minerotrophic peats being offset by greater P immobilisation owing to geochemical sorption (Bridgham et al., 1998).

CH_4 oxidation is also affected by nutrient additions. Bodelier (2011) reported a decrease in CH_4 oxidation by 38% on average in wetland and upland soils that were fertilised with N additions ranging between 10 to 560 kg N ha^{-1} yr^{-1}. Bodelier (2011) attributed this decease in methanotrophy to either inhibition of the process or the occurrence of anammox transformations consuming CH_4 produced via methanogenesis. Increased NH_4^+ concentrations can induce anammox transformations if either NO_2^- or NO_3^- are present. CH_4 can also be used by anaerobic ammonium oxidising bacteria as the two

molecules are very similar and oxygenase enzymes tend to be non-specific (Smemo and Yavitt, 2011), thus reducing CH_4 concentrations.

A number of studies have found that increasing NO_2^- and NO_3^- concentrations by fertilisation augmented N_2O emissions between 0.5 and 215 % depending on concentrations added and the environment they were added (Nykanen et al., 2003, Liu and Greaver, 2009), due to increased rates of nitrification and denitrification. NO_2^- additions provide substrates for nitrification and subsequently denitrification to occur, producing N_2O in lower soil moisture environments and N_2 in higher moisture environments (section 2.3.1.2). NH_4^+ additions have also been shown to increase N_2O production (Nykänen et al., 2002), either by anammox or ammonification and subsequently nitrifier-denitrification or nitrification and denitrification (section 2.3.1.2).

2.3.4.3 NO_3^- as an e^- acceptor

NO_3^- has been found to act as an electron acceptor in microbial processes. An example is in anaerobic CH_4 oxidation, which has been well reported within marine sediments (Smemo and Yavitt, 2011). Normally within marine environments, SO_4^{2-} is used as a final electron acceptor in the following reaction (Knittel and Boetius, 2009):

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \qquad \text{Eq. 9}$$

However, there is the potential for this process to occur in other environments, such as peatlands (Smemo and Yavitt, 2011), which represents a significant CH_4 source and forms under anaerobic conditions.

It has been suggested that NO_3^- could be used in peatland to anaerobically oxidise CH_4, as NO_3^- is more energetically efficient than SO_4^{2-} (Smemo and Yavitt, 2011), especially in low-SO_4^{2-} environments. Work has been undertaken by Raghoebarsing et al. (2006) and Ettwig et al. (2010) to establish whether there is a link between CH_4 and the N cycle. They found that the reaction is thermodynamically feasible when coupled with denitrification (Eq. 10, Figure 5 and Figure 6) (Ettwig et al., 2010).

$$3CH_4 + 8NO_2^- + 8H^+ \rightarrow 3CO_2 + 4N_2 + 10H_2O \qquad \text{Eq. 10}$$

$$(\Delta G^{\circ\prime} = -928 \text{kJ mol}^{-1}\ CH_4)$$

CH_4 acts as the electron donor for either NO_2^- (as shown in Eq. 10) or NO_3^- ($\Delta G°' = -765 kJ\ mol^{-1}\ CH_4$; Raghoebarsing et al., 2006), so that denitrification can occur and produce NO, N_2O or N_2 (Ettwig et al., 2008). .

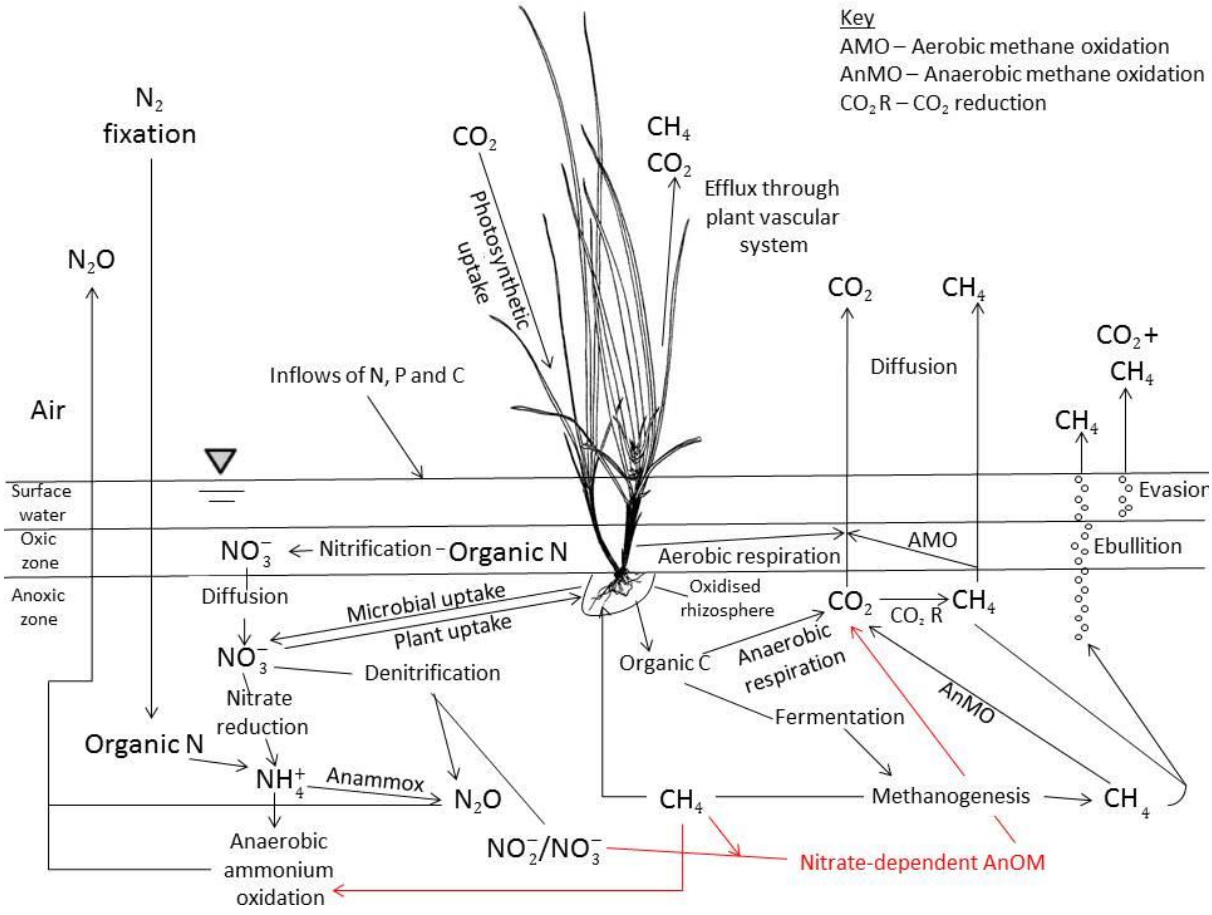


Figure 5 C-N interactions in GHG production

There are also a number of problems related to this process. Firstly, a well-established denitrifying population is needed for the processes to occur (Smemo and Yavitt, 2007). Additionally, abundant NO_2^- or NO_3^- is needed, which is often not the case in peatlands (Smemo and Yavitt, 2007). Therefore, NO_2^- and NO_3^- concentrations may limit the rates of anaerobic CH_4 oxidation coupled with denitrification, due to their fast N cycling and uptake by vegetation and microbes. Furthermore, it is also important to note that NO_2^- and NO_3^- are CH_4 inhibitors (see section 2.3.4.2), thereby reducing the concentrations of CH_4 available for oxidation.

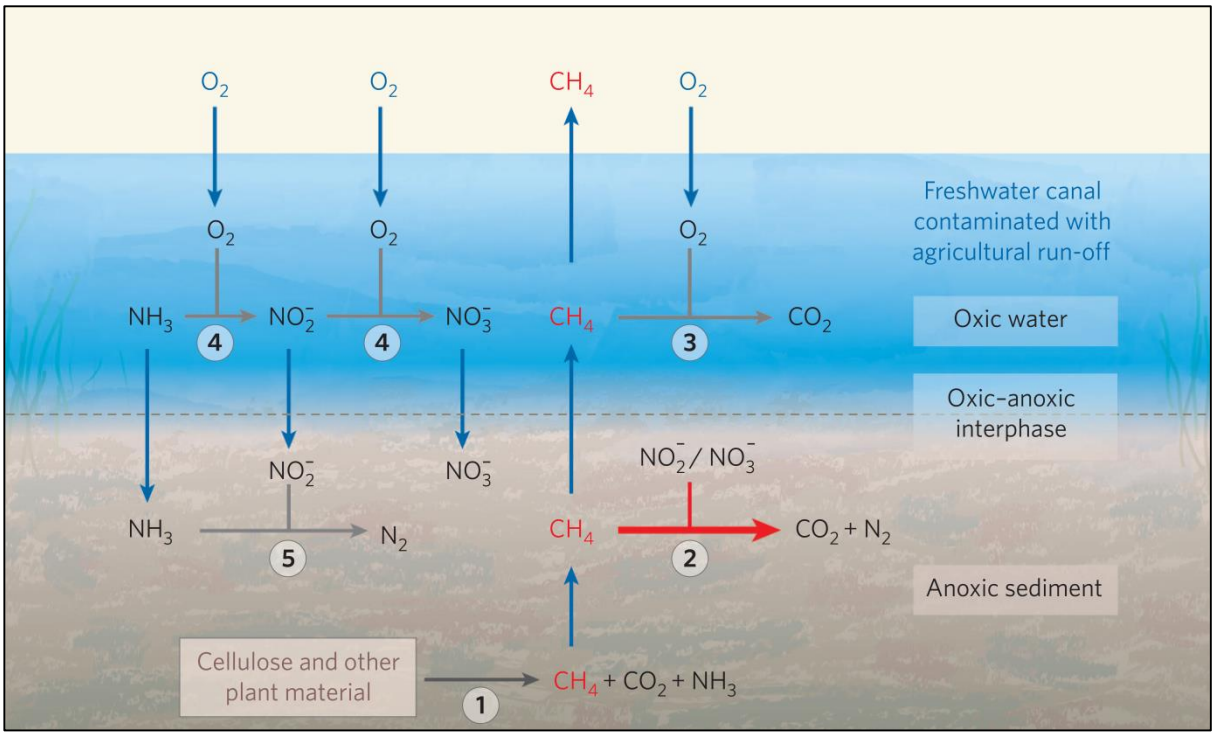


Figure 6 Nitrate-dependent anaerobic oxidation of methane (Thauer and Shima, 2006, p.878). Processes (grey and red arrows) involved are undertaken by: 1. Anaerobic bacteria, protozoa and archaea; 2. Archaea related to methane-producing archaea and bacteria; 3. Methane-consuming bacteria; 4. Nitrifying bacteria; and 5. Planctmycete bacteria.

2.4 Summary and synthesis

Peatlands are large stores of C and have the potential to be either a significant sink or source of atmospheric C. Floodplain fens are unique environments due to their lowland location, vegetation, hydrology and chemistry. These same biotic and abiotic factors are also key controls on biogeochemical cycling and GHG exchange within these environments. Little work has been done to quantify GHG exchange within floodplain fens in the UK, despite the possibility of these sites potentially being significant sources of GHGs. From research conducted in other countries like Germany and The Netherlands, fluxes from floodplain fens are significantly greater than upland ombrotrophic bogs. It is necessary to quantify GHG fluxes from these environments to have a complete picture for national GHG inventories.

Additionally, little is known about alterations to biogeochemical cycles from fluvial nutrient inundation. Research conducted in other environments and on atmospheric N and P

deposition on floodplain fen peat in The Netherlands have shown alterations to C and N cycles and to GHG exchange. Taking the effects of N and P alterations to C and N cycling from simulated atmospheric deposition, there is a large possibility that fluvial nutrient inputs to floodplain fens can significantly alter GHG exchange and needs to be researched.

2.5 Research questions

In order to ascertain the impacts of nutrient loading on GHG exchange in floodplain fens, the following research questions (R.Q.) will be investigated. A rationale and approach for each hypothesis are also listed below.

R.Q.1. What is the nutrient status of Sutton and Strumpshaw fens? (Chapter 3)

H_1: Strumpshaw Fen will have greater peat N and P contents than Sutton Fen.

H_2: Strumpshaw Fen will have greater foliar N and P contents than Sutton Fen.

H_3: Strumpshaw Fen will have greater porewater NO_3^- and SRP concentrations than Sutton Fen.

Rationale: Greater peat, vegetation and porewater N and P concentrations will result in greater photosynthesis, respiration and methanogenesis rates due to larger aboveground plant biomass to photosynthesise and more reactants available for microbes to undertake mineralisation processes.

Approach: 3 m peat cores, plant leaves and porewater samples will be collected during the 16 month sampling period and analysed for N and P contents/concentrations to establish a difference in nutrient status between the two sites. Foliar ratios will be used to assess differences in vegetation nutrient limitation.

R.Q.2. How do CO_2 and CH_4 fluxes from Sutton and Strumpshaw Fen compare to European floodplain fens? (Chapter 4)

Rationale: Little research has been conducted on GHG exchange within floodplain fens in the UK. The magnitude of these fluxes are not currently known. As ombrotrophic bogs have different controlling factors on C exchange, fluxes from Sutton and Strumpshaw Fen will be compared with other floodplain fen studies. The majority of research

published within the literature on temperate floodplain fens has been undertaken in Europe.

Approach: A 16 month sampling period will be used to quantify CO_2 and CH_4 exchange at two floodplain fen sites under conservation management, which will then be contextualised within the floodplain fen literature.

R.Q.3. What are the controlling factors on CO_2 and CH_4 exchange from floodplain fens? (Chapter 4)

H_4: R_{eco} will be controlled by peat temperature, VGA, water level and porewater NO_3^- and PO_4^{3-} concentration.

H_5: GPP will be controlled by air temperature, PAR, VGA, water level and porewater NO_3^- and PO_4^{3-} concentration.

H_6: CH_4 emission will be controlled by peat temperature, VGA, water level, redox conditions, barometric pressure, and porewater NO_3^- and PO_4^{3-} concentration.

Rationale: Based on literature findings, R_{eco}, GPP and CH_4 fluxes are influenced by a number of different controlling factors.

Approach: Mixed-effects modelling will be used on data obtained in R.Q.2 to establish controlling factors on R_{eco}, GPP and CH_4 fluxes.

R.Q.4. What are the averaged hourly episodic ebullition rates from the two floodplain fens? (Chapter 5)

H_7: Averaged hourly episodic ebullition rates will be greater at Strumpshaw Fen than Sutton Fen.

Rationale: The more nutrient enriched site will produce more CH_4 due to more reactants being available for methanogens to mineralise OM.

Approach: A 16 month sampling period will be used to quantify ebullition rates at two floodplain fens.

R.Q.5. Over a one year period, what are the integrated annual fluxes for CO_2 and CH_4 and their intra-annual variability from the two floodplain fens? (Chapter 6)

H_8: Strumpshaw Fen will have greater annual fluxes for GPP, R_{eco} and CH_4.

Rationale: The higher nutrient status at Strumpshaw Fen will result in greater aboveground biomass that can sequester CO_2, as well as produce and emit more C due to higher microbial biomass and activity.

Approach: Integrated annual fluxes for CO_2 and CH_4 will be calculated using mixed effects infill modelling techniques on data obtained in R.Q.2.

R.Q.6. What are the CO_2-equivalent GHG fluxes for each GHG for Sutton and Strumpshaw fens? (Chapter 6)

H_9: CH_4 will have a greater CO_2-equivalent flux than CO_2 at both sites.

Rationale: The saturated conditions that occur within floodplain fens provide anaerobic conditions for methanogenesis.

H_{10}: Strumpshaw Fen will be a greater sink of CO_2 than Sutton Fen.

Rationale: The higher nutrient status at Strumpshaw Fen will cause greater CO_2 uptake, due to a larger aboveground biomass.

Approach: Annual CH_4 fluxes from R.Q.5 will be transformed into CO_2-equivalent fluxes. Comparisons between annual NEE from R.Q.5 and a total CO_2-equivalent flux will be made between sites.

R.Q.7. How does potential production of CO_2, CH_4 and N_2O change with fertilisation of N and P loads in nutrient-rich and nutrient-poor floodplain fen peat? (Chapter 7)

H_{11}: Potential CO_2, CH_4 and N_2O production will be greater in nutrient-rich than in nutrient-poor peat.

Rationale: Greater nutrient availability in the nutrient-rich peat will result in higher reactant availability for fermentation, methanogenesis and denitrification.

H_{12}: NPG fertilisation will increase potential CO_2 and N_2O production rates more than other treatments.

Rationale: Microbes are often nutrient limited and the addition of NPG will allow greater rates of fermentation and denitrification to occur.

H_{13}: PG fertilisation will increase potential CH_4 production rates more than other treatments the most.

Rationale: Methanogens are often nutrient limited and the addition of PG will increase potential production as greater reactants will be available.

Approach: An *ex situ* 15 day fertilisation microcosm experiment will be undertaken on peat taken from the delineated research areas at Sutton and Strumpshaw Fen.

3. Site description and nutrient status

This chapter describes the two sites chosen to quantify greenhouse gas exchange and presents data on the nutrient status of the two sites (R.Q.1), testing the following hypotheses:

H_1: Strumpshaw Fen will have greater peat N and P contents than Sutton Fen.

H_2: Strumpshaw Fen will have greater foliar N and P contents than Sutton Fen.

H_3: Strumpshaw Fen will have greater porewater NO_3^- and SRP concentrations than Sutton Fen.

A site in a larger agricultural catchment has the potential to receive more nutrients from the rivers that inundate the site. Differences in nutrient status at these sites will be driven by the rivers that inundate them and will cause differences in vegetation and microbial populations and processes.

The two sites selected for this research are outlined in section 3.1. The methods used to establish nutrient status are outlined in section 3.2. Vegetation and peat physical and chemical properties and porewater nutrient concentrations are presented in section 3.3, followed by a discussion of nutrient status in order to establish differences between the two selected sites for R.Q.1 (section 3.4).

3.1 Site description

The Norfolk Broads are an internationally recognised wetland complex that is made up of a number of slow flowing rivers, interconnected by a number of broads. The broads are shallow lakes formed by the inundation of Medieval peat cuttings (Lambert et al., 1960). There are approximately 3300 ha of undrained peatlands in the broadlands, formed due to the poor natural drainage of the river floodplains (Wells and Wheeler, 1999). Two sites under conservation management were selected within the Norfolk Broads, a nutrient-poor floodplain fen, Sutton Fen, and a nutrient-enriched fen, Strumpshaw Fen (Figure 7). Previous studies on the two sites have indicated potential differences in nutrient status (Moss, 1979, Osborne, 1981, Haycock and Lamberth, 2000, Surridge, 2004, Surridge et al., 2007).

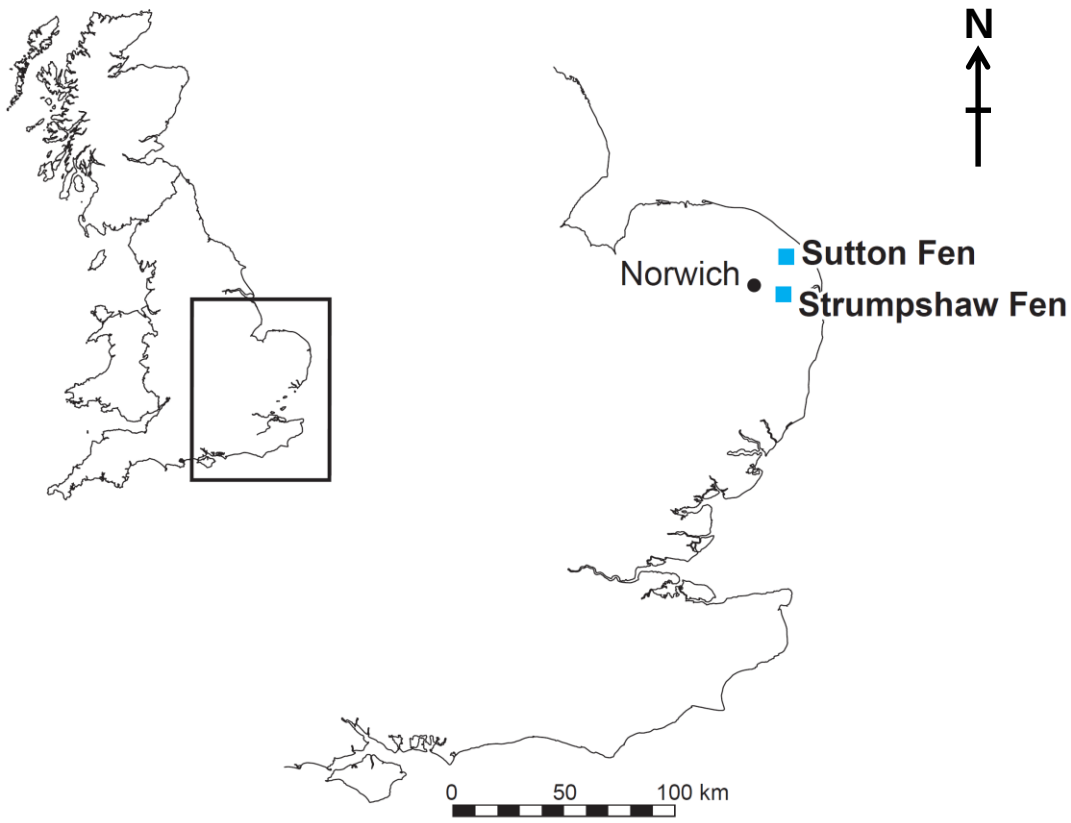


Figure 7 Location map of Sutton and Strumpshaw Fen.

3.1.1 Sutton Fen

Sutton Fen is a floodplain fen located approximately 20 km northeast of Norwich (52°45′N 001°30′E) within the predominantly arable catchment of the River Ant. It forms part of the Ant Broads and Marshes Site of Specific Scientific Interest (SSSI) and is a National Nature Reserve (NNR) managed by the Royal Society for the Protection of Birds (RSPB). The area is also a Ramsar site and a Special Area of Conservation (pSAC) under the EC Habitats Directive. The site was selected due to its poorer nutrient status (Mason, Pers. comm.). It was acquired by the RSPB in 2006 and had previously been maintained as a floodplain fen since it was last dug for peat in the 13th and 14th centuries (Mason, Pers. comm.). The River Ant runs to the eastern edge of Sutton fen and Sutton Broad lies to the north. A low bank surrounds the fen, with sluice gates in the north-eastern corner and on the western bank. The sluice gates were last opened in 2010 when the water levels in the fen's ditches were extremely low, in order to increase the water level and reduce water stress on the fen. However, water from the river frequently enters the fen via leaks in the bank and by overtopping of the banks surrounding the fen.

Sample collection took place within an area dominated by reeds (last cut in 2009) in the middle of the fen, away from the river and broad, to ensure that the area was nutrient poor. Common plant species found within the fen include reeds and grasses (*Phragmites australis* (Cav.) Trin. ex Steud (1841), and *Calamagrostis canescens* (Web.) Roth (1789)) and sedges (*Carex acutiformis* Ehrh. (1789) and *Cladium mariscus* (L.) Pohl (1809)), as well as other vascular plants, including *Berula erecta* (Huds.) Coville (1893), *Galium palustre* L. (1753), *Hydrocotyle vulgaris* L. (1753), *Juncus subnodulosus* Schrank (1789), *Lysimachia vulgaris* L. (1753), *Mentha aquatica* L. (1753), *Myrica gale* L. (1753), *Peucedanum palustre* (L.) Moench (1794), *Scutellaria galericulata* L. (1753), *Thelypteris palustris* Schott (1834) and *Typha latifolia* L. (1753) (Broads Authority, 2010). The reed beds in the fen are cut on a 5/7 year rotation, with vegetation being burnt on site and the ashes removed as to retain the poor nutrient status (Mason, Pers. comm.).

3.1.2 Strumpshaw Fen

Strumpshaw fen is located in the River Yare's northern floodplain, approximately 10 km southeast of Norwich (52°36′N 001°27′E). The site forms part of the Yare Broads and Marshes SSSI and is a NNR under the management of the RSPB since 1975. The River Yare flows to the east of the fen and the Lackford Run to the north. Both rivers provide water to the fen through bank seepage and through a sluice gate located in the northeast corner of the fen, which is opened in December to flood the site. The site was selected due to the higher phosphorous (P) peat content of the fen caused by the nutrient rich waters from the River Yare and the Lackford Run, which has a history of high P inputs from a sewage treatment[1] upstream of the fen (Haycock and Lamberth, 2000, Surridge, 2004). The River Yare and the Lackford Run are in catchments with high arable farming activity and have a tidal influence, with an increase in water levels in the rivers around Strumpshaw Fen at high tides.

Strumpshaw Fen is managed on a 7-8 year rotation, with reed and sedge cutting and scrub removal. Vegetation is burnt onsite and left on the fen as the fertilisation effect of the ash does not significantly alter the nutrient status as the peat has high nutrient contents from historical inputs (Strudwick, Pers. comm.). The ditch network within the site is maintained on a 2 year cycle, removing vegetation and reshaping ditches. The water level in the fen is also managed, with water levels maintained at the peat surface through the use of sluice gates to inundate the fen with river water. The sluice gates are

[1] P was not removed from the sewage treatment plant until it was closed in 1997 (Haycock and Lamberth, 2000).

generally opened once a year in the winter to supplement the water level (Strudwick, Pers. comm.).

Sampling took place in an area dominated by reed cut in 2009. A number of ditches interconnected with the Lackford Run are in close proximity to the sampling area. Common plant species found within the site include reeds and sedges (*P. australis*, and *C. canescens*, *Phalaris arundinacea* L. (1753), *C. acutiformis* and *C. mariscus*) (Broads Authority, 2010). Other vascular plants found within the site include *B. erecta, Calystegia sepium* (L.) R. Br. (1810), *Eupatorium cannabinum* L. (1753), *G. palustre, H. vulgaris, J. subnodulosus, L. vulgaris, M. aquatica, M. gale, P. palustre, Rumex hydrolapathum* Hudds. (1778), *T. palustris* and *T. latifolia* (Broads Authority, 2010).

3.1.3 Sampling approach

In order to answer R.Q. 1 to 4, areas dominated by *P. australis* that were cut in 2009 were chosen within Sutton (Figure 8) and Strumpshaw Fen (Figure 9) to ensure comparability between sites. The area chosen in Sutton Fen (nutrient-poor site) was located within the middle of the fen (Figure 8) to guarantee nutrient poorer conditions and eliminate the impact of fluvial nutrient encroachment via bank seepage. Contrastingly, the area at Strumpshaw was selected due to its proximity to the drainage ditch connected to the Lackford Run (Figure 9).

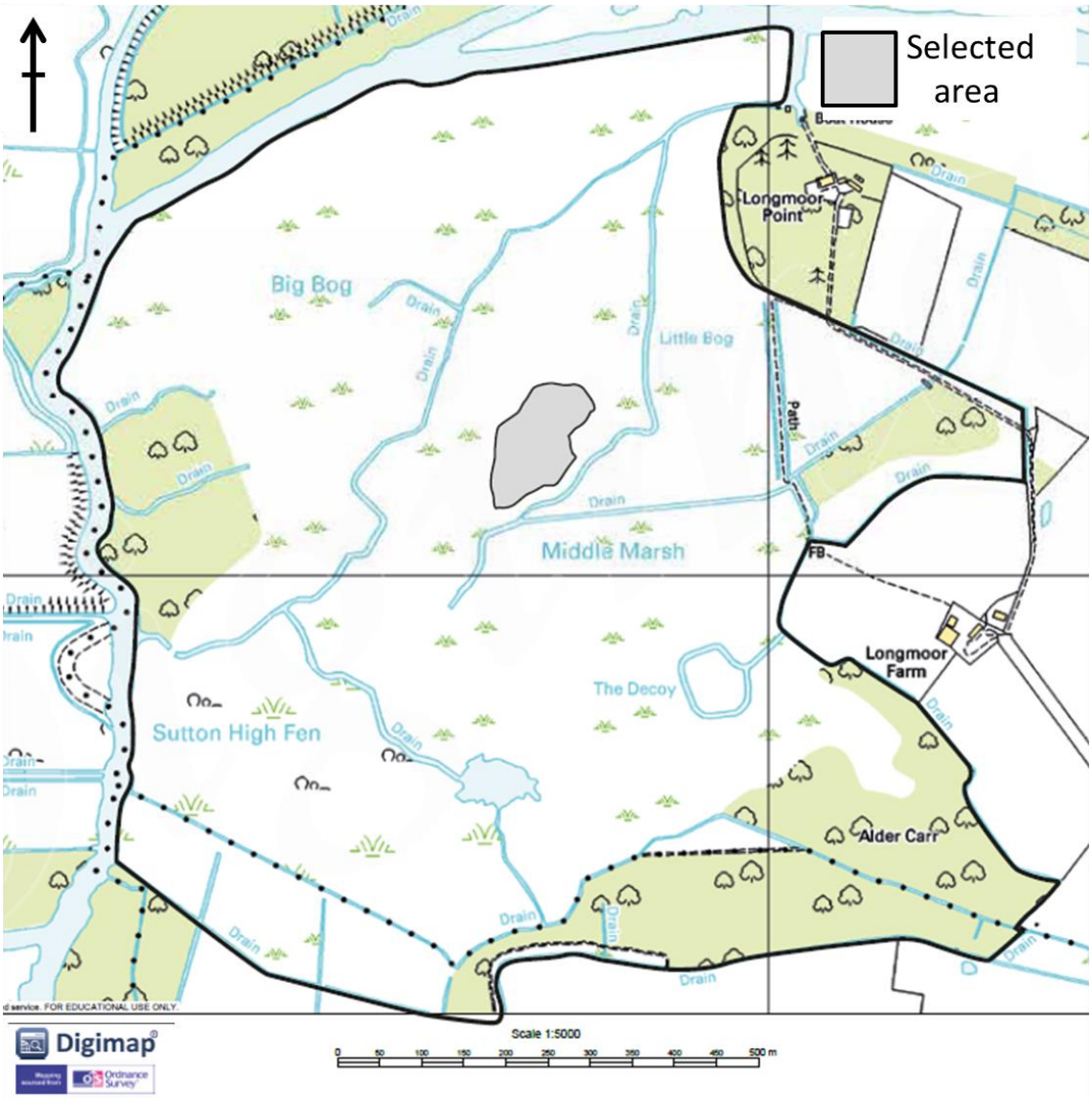


Figure 8 Selected sampling site location at Sutton Fen

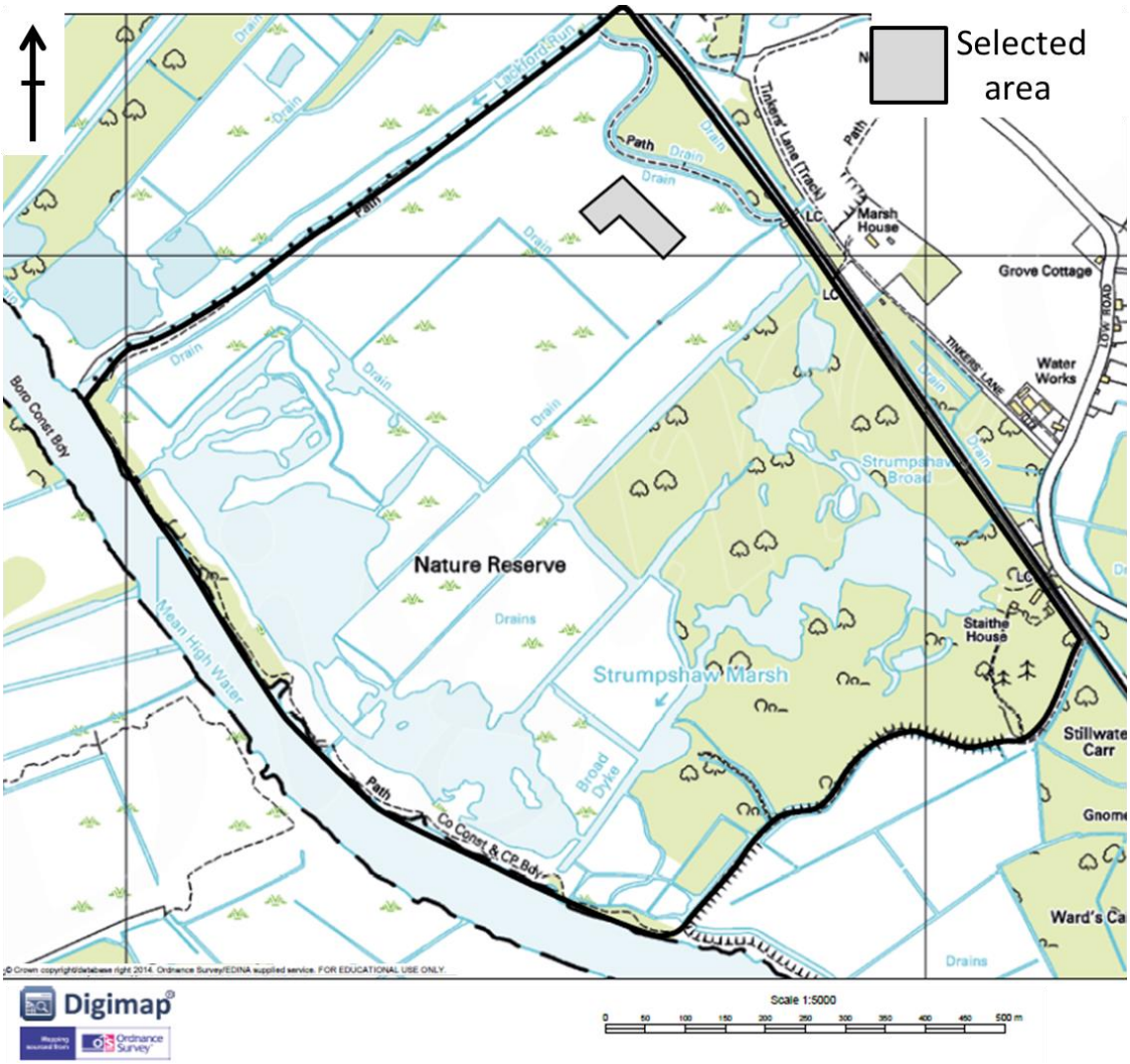


Figure 9 Selected sampling site location at Strumpshaw Fen

To measure GHG exchange at the sites, a tall static chamber method was chosen (see section 4.2 for further details; Figure 10A). This method requires a collar, a static structure sunken into the ground for the chamber to sit upon (Figure 10B). At Sutton and Strumpshaw Fen, 6 collars were inserted into the peat at each site to try to capture site variability in GHG emission. Each pair of collars were inserted in pairs 10 m apart from each other, as to reduce the amount of disturbance during sampling, within the selected sampling area. However, each collar was treated individually. Locations for the collars were chosen to best represent the vegetation of the selected area. An inverted glass funnel (see section 3.4) to collect ebullitive fluxes and a monitoring well (see section 4.2.4) were also located within a 1 m radius of each collar. An automatic weather station (see section 3.2.7) and barologger (see section 3.2.7) were also located within close proximity to the selected monitoring areas, along with a photosynthetically active

radiation (PAR) meter at Sutton Fen. Site schematics for Sutton and Strumpshaw Fen are shown in Figure 11 and 12, respectively.

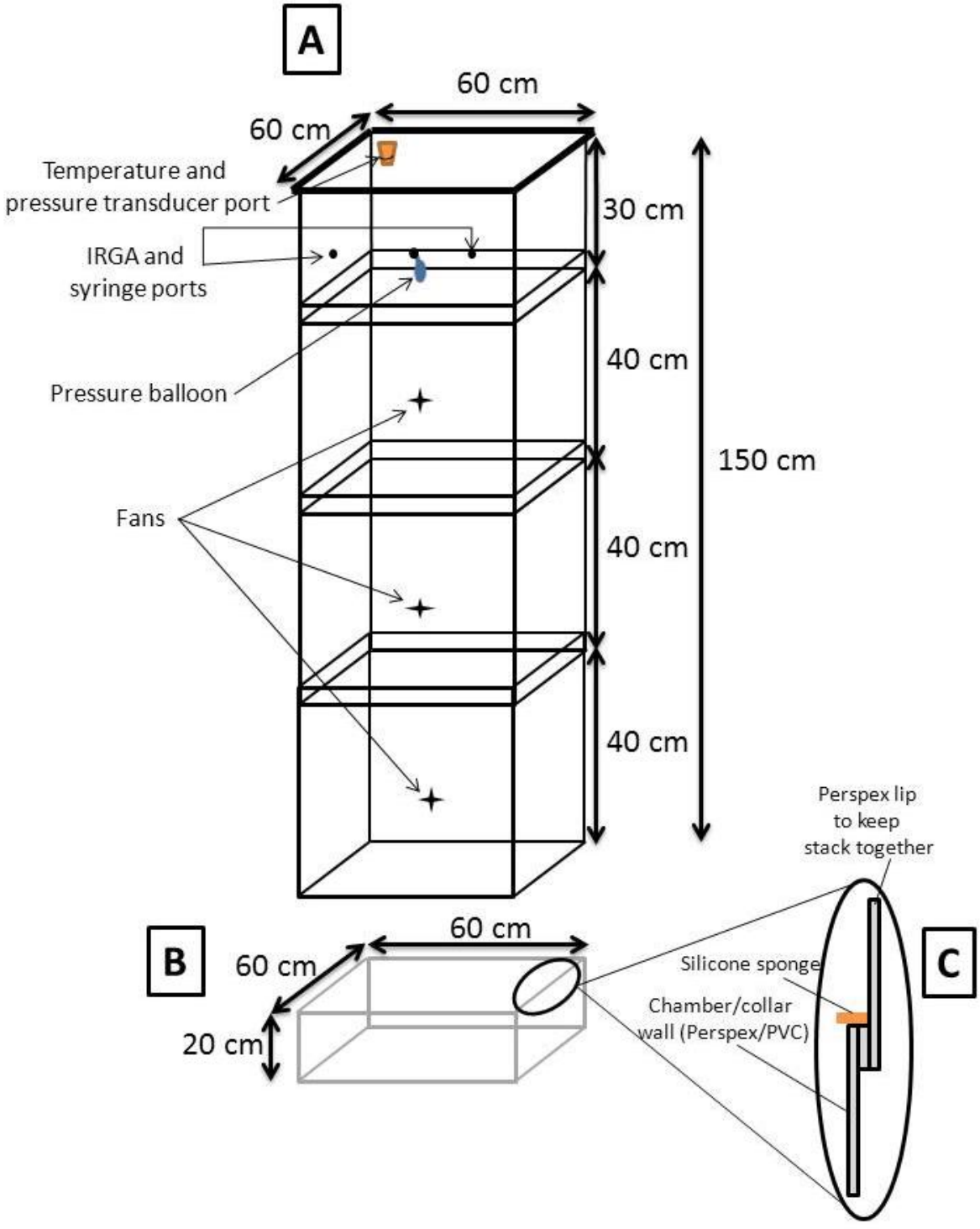


Figure 10 Tall closed chamber design (not to scale), including: A. Segmented closed chamber, B. Collar and C. Silicone sponge seal at the top of each section

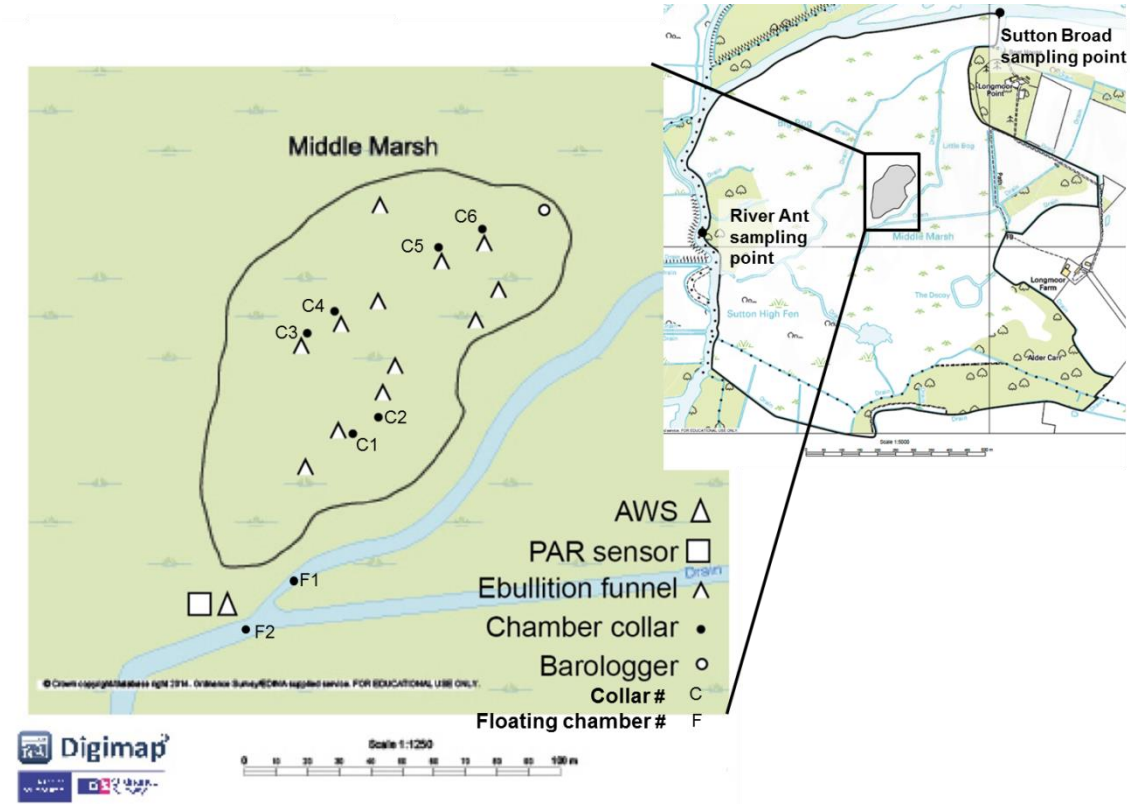


Figure 11 Site schematic for Sutton Fen

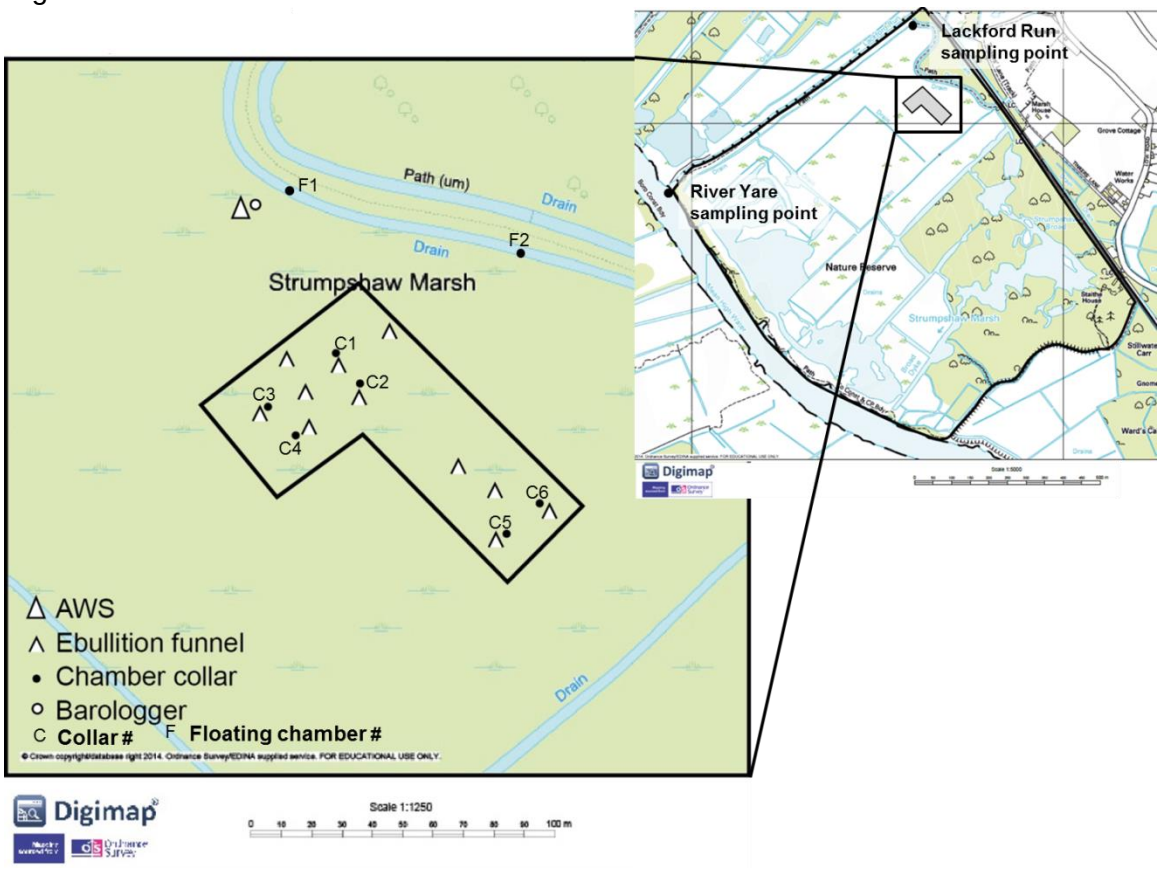


Figure 12 Site schematic for Strumpshaw Fen

Two ditches close to the sampling areas at each site were also chosen to measure ditch GHG exchange and water chemistry. These locations (shown in Figure 11 and 12 for Sutton and Strumpshaw Fen, respectively) were chosen for proximity to the sampling location, ease of access and permanency of access throughout the 16 month sampling period. Ditch water samples were taken adjacent to where floating chamber GHG exchange measurements were taken in order to give representative water chemistry concentrations. Fen ponds were not investigated due to issues with sampling techniques. Access to areas within the ponds to sample is difficult without disturbing the surface water-atmosphere boundary layer and inducing human-induced evasion. Additionally, site access issues due to nesting birds prevented the quantification of evasion from fen ponds. There is a potential for fluxes from ponds to be greater than ditches due to the larger surface area and a lack of shelter from the surrounding vegetation allowing greater disturbance of the surface water-atmosphere boundary layer and inducing evasion.

For both sites, a location on both of the rivers/water bodies that run adjacent to the site (Sutton Fen: River Ant and Sutton Broad; Strumpshaw Fen: River Yare and Lackford Run) was chosen to sample river water physicochemistry. These locations (shown in Figure 11 and 12) were chosen for their influence on the site, often coinciding with a sluice gate where water is allowed in to inundate the site when necessary, depending on the site management.

3.2 Site nutrient status methodology

To ascertain the difference in nutrient status between the two sites, peat, vegetation and pore-, ditch and river water nutrient contents/concentrations were investigated. The methods used are presented within this section.

3.2.1 Peat composition

To ascertain the structure, botanical composition, stratification and state of humification of the peat, 15 cores were taken at each site using a grid system within the selected areas at both sites. Each 3 m core was collected using a 2.5 cm gauge auger, paying attention not to cause any compaction. A number of other methods, including cutting the peat to fit in a box with removable sides and a Russian corer were tested; however these methods did not work well throughout the peat profile. The cores were split into 5 cm sections for the first 20 cm, then every 10 cm (0.2 - 1 m depth) and then every 50 cm thereafter, using a knife. The von Post method was used to ascertain the state of

humification as it is a quick field based technique and due to its wide scale use in peatlands (Shotyk, 1988, Chambers et al., 2011). The Troels-Smith technique was used to describe stratification (Troels-Smith, 1955, Kershaw, 1997) within the peat profile, whilst the peat colour was noted using a Munsell chart. The peat darkness, elasticity and structure was determined using a numeric scale of 0 – 4, as in Kershaw (1997).

3.2.2 Peat physicochemistry

The peat chemistry was established at each site by taking triplicate cores at 3 locations to a depth of 3 m (n = 9). Triplicate cores were taken to ensure enough material was collected for analysis and were taken over a small sampling area (< 20 cm^2). Each 3 m core was split as described previously (section 3.2.1). The sub-samples of the first of each triplicate were placed in a bag along with 10 mL of deionised water to create a slurry to measure the pH of the peat profile *in situ* using a calibrated portable pH meter (VWR pH 100). The sub-samples from the two remaining cores of each triplicate were double bagged and returned to the laboratory. One of the cores was used to ascertain carbon (C), nitrogen (N), phosphorus (P) and potassium (K) contents using an elemental analyser (C & N) and inductively coupled plasma spectroscopic analysis (P & K; section 3.2.5). Sub-samples from this core were freeze dried and ground using a ball mill to homogenise the sample. The final core was used to ascertain bulk density and loss on ignition (LOI). Sections from the peat profile were weighed, dried in the oven at 70 °C until a constant weight (Chambers et al., 2011). Bulk density was calculated using the following equation:

$$P = \frac{M_{dry}}{V} \qquad \text{Eq. 11}$$

where P is the bulk density (g cm^{-3}), M_{dry} is the mass of dry peat (g) and V is the total volume of the core section (cm^3).

Bulk density samples were then placed in a muffle furnace at 550 °C for 4 hours to oxidise all organic matter (Chambers et al., 2011). Samples were then reweighed once cooled to calculate LOI, using the following equation:

$$Q = \frac{(M_{dry} - M_{muffled})}{M_{dry}} \cdot 100 \qquad \text{Eq. 12}$$

where Q is the LOI (%), M_{dry} is the mass of dry peat (g) and $M_{muffled}$ is the mass of the muffled peat and 100 is a conversion factor to a percentage.

3.2.3 Vegetation CNPK content

Ratios of foliar CNPK contents have been used as a means of assessing nutrient limitation in vegetation (Gusewell et al., 2003, Olde Venterink et al., 2003, Tessier and Raynal, 2003, Gusewell, 2004). CNPK contents were determined by collecting 10 leaves from each species observed in each collar from within 2 m of each collar in September 2012. Collection of leaves from within the collars would have been destructive to the above-ground biomass and problematic to GHG measurements, hence the collection of material from close to the collars. All plant species were pooled together for each collar, but were not weighted for difference in species abundance or biomass. Analysing each species individually would have been too time intensive and would have cost too much to make it feasible for this study. Only a representative total foliar CNPK content per collar was required for the foliar ratio method. Samples were freeze dried and ground using a ball mill (Olde Venterink et al., 2003). Samples were then analysed using elemental analysis and inductively coupled plasma spectroscopy (section 3.2.5). Ratios of plant N, P and K were compared to nutrient limiting ratios in the literature (Table 3).

Table 3 Foliar macronutrient ratios from Olde Venterink et al. (2003) and Gusewell (2004)

N limited	N:P < 14.5, N:K < 2.1
P limited	N:P > 14.5, K:P > 3.4
K limited	N:K > 2.1, K:P < 3.4

3.2.4 Vegetation survey

The vegetation for each collar and 18 quadrats within the sampling area at both sites was surveyed at peak biomass in September 2012 at both Sutton and Strumpshaw Fen by a plant ecologist (Dr Andrew Skinner) from the RSPB. Plant species abundance was measured using the Domin scale (Currall, 1987) for each collar and three 0.5 x 0.5 m quadrats within a 3 m radius of each collar. An average plant height was also measured and used as a proxy for difference in nutrients between sites. As the Domin scale provides data handling and interpretation problems, data was then transformed to a percentage using the following equation (Currall, 1987):

$$C = \frac{D^{2.6}}{4} \qquad \text{Eq. 13}$$

Where *C* is the species cover as a percentage, *D* is the species cover using the Domin scale and 2.6 and 4 are conversion factors.

The productivity of each fen was also assessed at each site, using above-ground green biomass as a proxy for productivity (Olde Venterink et al., 2003). Standing above-ground green biomass was harvested at peak biomass in September 2013, cutting the vegetation near the peat surface in 10 quadrats (0.5 x 0.5 m). Litter on the surface was not included. Samples were air dried to a constant weight and the weight was recorded. Above-ground green biomass weights were then transformed to g m^{-2}.

3.2.5 Chemical analysis of peat and vegetation

The nutrient content of peat and plant leaves were ascertained using elemental analysis for C and N, and inductively coupled plasma optical emission spectroscopy (ICP-OES) for P and K (Syed et al., 2006). For the elemental analyser (EA), all equipment was acid washed in 10% HCl. Dried and ground peat samples were weighed out into tin boats and weights were recorded in grams to 6 decimal places. 5 differing weights of aspartic acid (10.52% N and 36.09% C; Thermo Scientific) were used to create a calibration sequence, with each weight being recorded in grams to 6 decimal places. Aspartic acid was also used for analytical drift checks. Empty tin boats were used as laboratory blanks. Two certified reference materials (CRM) were used: Wepal ISE 865 (loam soil; 40 g kg^{-1} C and 3.31 g kg^{-1} N; Wageningen University, The Netherlands) and Wepal IPE 176 (*P. australis*; 332 g kg^{-1} C and 8.08 g kg^{-1} N; Wageningen University, The Netherlands). Average recoveries for the EA are shown in Table 4. Recoveries were rejected if < 90 % or > 110 %.

Table 4 EA CRM % recovery for Wepal ISE 865 and Wepal IPE 176.

CRM	C	N
Wepal ISE 865 (loam soil)	99	98
Wepal IPE 176 (*Phragmites australis*)	98	100

An Aqua Regia digest was used to extract P and K from peat and plant leaf samples before ICP-OES analysis (Syed et al., 2006). For the digest, all glassware was washed in 10 % HNO_3 and rinsed in deionised water. Around 0.5 g of sample was weighed out into an Erlenmeyer flask with a reflux ball and 12 mL of Agua Regia (3:1 v/v HCl:HNO_3) was added to each sample (Syed et al., 2006). Samples were then heated on a hotplate for three hours at a rolling simmer. Samples were left to cool, filtered through a toughened filter paper (Whatman) into a 50 mL volumetric flask and diluted to 50 mL

volume using ultrapure water (UHQ[2]). Samples were then transferred to 50 mL centrifuge tubes and stored at 4 °C until analysis. Three CRMs were used to check digest recoveries: Wepal ISE 865 (loam soil; 512 mg kg^{-1} P and 2010 mg kg^{-1} K; Wageningen University, The Netherlands), Wepal IPE 176 (*P. australis*; 1280 mg kg^{-1} P and 13000 mg kg^{-1} K; Wageningen University, The Netherlands) and NIMT/UOE/FM/001 (Ombrotrophic peat; 281 mg kg^{-1} P; National Institute of Metrology, Thailand). CRMs were digested using the same method for the samples. A laboratory blank of only 12 mL Aqua Regia was also used to assess contamination.

Standards to create a nine point calibration sequence for the ICP-OES were made up from individual 1000 ppmv P and K calibration solutions (Fisher Scientific). Standards were diluted with Agua Regia and UHQ to produce a 24 % Aqua Regia solution to match the matrix of the samples. The 2 ppm standard was also used as a laboratory drift control. All samples, standards and drift checks were then spiked with 100,000 mg L^{-1} Cs to supress easily ionisable elements (Todolí et al., 2002). A linear regression was used to create a calibration curve for each run on the ICP-OES. Recoveries were assessed after each run and rejected if < 90 % or > 110 %. Average recoveries for the ICP-OES are shown in Table 5.

Table 5 ICP average CRM % recovery.

CRM	P	K
Wepal ISE 865 (loam soil)	101	95
NIMT/UOE/FM/001 (ombrotrophic peat)	93	N/A
Wepal IPE 176 (*Phragmites australis*)	104	93

3.2.6 Measuring water chemistry

Water chemistry was investigated in pore-, ditch and river water at both Sutton and Strumpshaw Fen over the 16 month sampling period. Samples were taken every month on site visits for GHG exchange sampling.

All glassware and equipment (syringes, filter holders and autosampler vials) were soaked in Decon and then rinsed with de-ionised water three times. Any glassware used for C

[2] UHQ was filtered to 18 MΩ cm^{-1} at 25 °C, Millipore Elix and Millipore synergy water systems.

analysis was then wrapped in aluminium foil and muffled in a furnace at 500 °C for 4 hours to ensure the full removal of any residual C. Spare foil was also muffled at the same time to be used as an intermediary barrier between the C vials and the polypropylene lids. Any equipment used during the sampling and analysis of N and P underwent the previous cleaning process but were soaked for a further 24 hours in 10% HCl and rinsed again in de-ionised water three times. Finally glassware and equipment were allowed to dry.

3.2.6.1 Sample collection

Porewater samples were taken from within 0.2 m radius of each collar using a stainless steel miniprobes (2 mm needle i.d., 40 cm long; Lansdown et al., 2014). A needle runs through the probe and at the base of the needle was packed with pre-washed[3] cigarette filters (Swann) to prevent the needle from blocking (Lansdown et al., 2014). The top of the needle had a 6 mm (i.d.) luer lock attachment to enable sample extraction (Lansdown et al., 2014). Probes were inserted adjacent to each collar to a depth of 30 cm as to be able to pull up porewater at any time of the year at both sites. 25 mL of porewater was extracted for porewater analysis from a theoretical sphere around the probe with a radius of 1.8 cm.

Ditch and river water samples were taken using a bailer (1 L polypropylene vial attached to a 1 m piece of polyvinyl chloride tubing). The bailer was rinsed three times with surface water, ensuring the waste was discarded downstream of the sampling point, before a sample was taken. Ditch water samples were taken from areas next to where floating chamber headspace sampling took place (Figure 11 and 12), so that ditch water concentrations were representative of the areas being sampled by the chambers. River water was sampled from specific point shown in Figure 11 and 12, which were decided upon at the beginning of the study based on access throughout the 16 month sampling period.

Dissolved inorganic and organic C (DIC and DOC, respectively) porewater samples were collected from each dipwell (section 4.2.4) using a syringe (Fisher Scientific) and a 1 m length of tygon tubing (i.d. 4mm). River and ditch water samples were taken using a bailer (described in section 3.2.6). For all pore-, ditch and river water samples, two 30

[3] Filters were washed using UHQ by packing the filters into the end of the probes, then pulling 30 mL UHQ through the probe and finally pushing 30 mL UHQ through the probe.

mL samples were filtered through a 0.45 μm membrane filter (Polysulphone, Whatman) for DIC and DOC. DOC samples were acidified to pH < 2 with 0.5 ml conc. HCl. DIC samples were not acidified. Samples then had muffled foil placed over the top and the lid was secured. Samples were stored in a cool box until returned to the laboratory, where they were refrigerated. pH, EC and DO were measured *in situ* using calibrated handheld meters (VWR pH100, VWR CO 310 and YSI 550A, respectively; VWR). For porewater samples, the probes were placed down the dipwells into the water and allowed to stabilise until a measurement was taken.

Pore- and ditch water dissolved gas samples were taken by transferring 10 mL of pore- or ditch water to a 25 mL gas-tight syringe with a lock valve (SGE Analytical Science, 25MR-VLLMA-GT). A 10 mL He headspace was then added to the sample and shaken for 1 minute to allow the equilibration of the headspace with the dissolved GHGs as in Hope (1995). The equilibrated saturated headspace was then transferred to a 3 mL exetainer filled with deoxygenated water, allowing the water to decant into a separate Duran bottle through a secondary needle. The samples were then stored until analysis in the laboratory.

Fe^{2+} was used as a proxy for pore- and ditch water redox state. Fe^{2+} samples were then taken by flushing a pre-washed (with 5 mL of UHQ) 0.2 μm polypropylene filter with 2 mL of sample to remove any oxygen present in the filter housing. 1.5 mL of sample was decanted into a vial with 1.5 mL of buffered phenanthroline (see Section 3.2.6.2 for preparation method) and stored until analysis in the laboratory.

N, P, SO_4^{2-} and Cl^- concentrations were quantified for pore-, ditch and river water. To allow for expansion when the sample was frozen, 11 mL of sample was filtered through a pre-washed (with 5 mL of UHQ) 0.2 μm polypropylene filter into a 12 mL vial for N, P, SO_4^{2-} and Cl^- analysis. Samples were chilled in the field and refrigerated upon return to the laboratory. A 0.2 μm filter was chosen for N and P sample filtration in order to remove any bacteria that would transform the macronutrient species and to remove colloidal forms of P that are not bioavailable and pass through 0.45 μm filters (Zak et al., 2004).

3.2.6.2 Laboratory analysis

DIC and DOC samples were analysed using UV-persulphate and combustion methods on a HiperTOC/TNb analyser. 1000 mg L^{-1} DIC and DOC stock solutions were made up from anhydrous sodium carbonate, anhydrous sodium carbonate and Analar grade sodium potassium hydrogen phthalate (Fisher Scientific), and standards and drift checks were made up by diluting the stock solution down in UHQ. DOC standards and drift checks were acidified with 0.5 mL concentrate HCl. A 9 part calibration curve was created from the standards and used to calculate sample concentrations. A certified reference material (DOC: QC1297-20ML lot 017494, RTC, Wyoming, USA) was run after the calibration standards. Drift checks and blanks were included every 10 samples for quality assurance purposes (Table 6). Field (UHQ passed through a filter following the protocol as above) and travel (UHQ decanted into a vial) blanks were also run for field quality assurance purposes. Results were rejected if drift was > ± 10 % and CRM recoveries were < 90 % or > 110 %.

Table 6 HiperTOC average RSDs (%) for analytical drift and % CRM recovery

	Drift	CRM
DOC	7.6	100.3
DIC	7.6	N/A

Dissolved gases were analysed using a Gas Chromatograph coupled with a Flame Ionization Detector and methanizer (GC-FID; Agilent Technologies 7890A GC system; zero grade N_2 carrier gas at 25 mL min^{-1}, zero grade H_2 (30 mL min^{-1}) and air (moisture and hydrocarbon-free; 400 mL min^{-1}) auxiliary gases, operated at 300°C; 1.8 m Propak Q chromatographic column with 80/100 mesh heated to 40°C and methanizer) and an Electron Capture Detector (ECD; Agilent Technologies 7890A GC system; Argon-Methane carrier gas at 30 mL min^{-1}; ECD run at 150 °C; 30 m capillary chromatographic column heated to 40 °C). Gas standards and drift checks were made up from an air mix (Scientific and Technical Gases Ltd – 98.7 ppm CH_4, 3706 ppm CO_2, 98.8 ppm N_2O) and diluted down using oxygen-free Nitrogen and Helium (BOC), taking temperature and barometric pressure into account. 3 mL of gas was injected into 3 mL exetainers (Labco Limited) prefilled with de-oxygenated water. Two lab air blanks were used at the beginning of each run to purge the machine of any gas that may have been left in the column. A seven point calibration was run, with a blank at the end of the calibration. Periodic drift checks (approximately every 10 samples; Table 7) were used to monitor the short-term drift of the machine. Headspace concentrations were calculated using the

area from the GC-FID/ECD and a linear regression was used to create a calibration curve. Results were rejected if drift was > 10 %. Bunsen coefficients were used to account for total CH_4 (Yamamoto et al., 1976), CO_2 (Weiss, 1974) and N_2O (Weiss and Price, 1980) in an aqueous and gaseous form in the sample-filled 3 mL exetainers, taking salinity into account.

Table 7 GC average RSDs (%) for 3 ml exetainer analytical drift

Detector	CO_2	CH_4	N_2O
FID	5.7	7.1	N/A
ECD	N/A	N/A	4.5

N and P species were analysed using an automated colorimetric continuous flow analyser (Skalar San++ continuous flow analyser). Stock solutions for NO_2^-, NO_3^-, NH_4^+ and SRP were made up from sodium nitrite, potassium nitrate, ammonium chloride and potassium dihydrogen phosphate (Fisher Scientific). A 7 part calibration was made up from standards diluted from the stock solutions with UHQ. A CRM (RTC simple nutrients, QCI 19S-20 ml) was run for quality assurance purposes, as well as drift checks (Table 8) and blanks approximately every 10 samples. Results were rejected if drift was > 10 % and CRM recoveries were < 90 % or > 110 %.

Table 8 Skalar average RSDs (%) for analytical drift and average CRM recovery rates (%)

	Drift	CRM
NO_3 (0.8 ppm-N)	6.6	101.9
NO_2 (0.8 ppm-N)	5.5	103.0
NH_4 (0.08 ppm-N)	6.5	99.1
PO_4 (0.08 ppm-P)	6.4	101.3

Cl^- and SO_4^{2-} were analysed using ion chromatography (Dionex ICS-2500 chromatographic system coupled with an ED50 electrochemical detector, GD50 gradient pump and AS50 autosampler). A 2 x 250 mm RFIC™ IonPac© AS18 column with an IonPac AG18 Guard column and an ASRS300 suppressor was used, with a 100 mM KOH eluent pumped at a flow rate of 0.25 mL min^{-1}. A 7 part calibration was made up from standards using UHQ and a stock 7 anion solution (Dionex II 057590 (09/08)). A

CRM (RTC Anions-WP, QCI - 051) was run for quality assurance purposes, as well as drift checks (Table 9) and blanks approximately every 10 samples. Results were rejected if drift was > 10 % and CRM recoveries were < 90 % or > 110 %.

Table 9 Dionex average RSDs (%) for analytical drift and average CRM recovery rates (%).

	Drift	CRM
Cl^- (100 mg L^{-1})	5.8	99.3
SO_4^{2+} (52 mg L^{-1})	6.9	96.3

Fe^{2+} was used as a proxy for redox conditions and measured using a spectrophotometer (Fisher Scientific). An Fe^{2+} stock solution was made up by adding hydroxyl ammonium chloride to a 50 ppm Fe standard (Fisher Scientific). Standards were made up by adding known concentrations of the stock solution to a phenanthroline buffer, made up using a phenanthroline solution (0.1 g 1-10 o-phenanthroline monohydrate powder in 100 ml of UHQ, Fisher Scientific) and an acetate buffer (16.59 g of anhydrous sodium acetate powder and 350 ml of UHQ and acidifying the buffer to pH 4 with analytical glacial acetic acid, Fisher Scientific). The buffer and solution were then mixed together but discarded if the solution turned a pale pink or orange colour due to Fe^{2+} contamination. A linear regression was used to create a calibration curve using the calibration sequence. Analytical drift was also measured throughout the sample analysis using the 2 ppm standard (average RSD).

3.2.7 Meteorological and environmental conditions

To investigate R.Q.1 to R.Q.6, meteorological data was required. Data was acquired using an on-site automated weather station (AWS; Skye Instruments MiniMet) that was located within the fen at both sites. Rainfall was measured using an ARG100 Tipping Bucket Rainguage that records data every 0.2 mm of rainfall. Incoming solar radiation was measured using a SKS 1110 Pyranometer and incoming and outgoing solar radiation was measured using a Net Radiometer. Photosynthetically Active Radiation was measured using a SKP 215 PAR Quantum Sensor (manufacturer's stated accuracy is > 97%). Air temperature and humidity were measured using a SKH 2070 RHT+ relative humidity and temperature probe (manufacturer's stated accuracy for temperature is ± 0.2 °C between 0 to 60 °C and better than 2 % for humidity), whilst substrate temperature was measured using a SKTS 200 Sheathed Temperature Probe (manufacturer's stated

accuracy of 0.1 °C). Wind speed and direction were measured using an A100R Switching Anemometer and a W200P/DI, respectively. The anemometer has an accuracy of 1 % of the reading for windspeeds between 10 and 55 m s^{-1}, 2% thereafter, and a threshold of 0.2 m s^{-1}. The wind vane is accurate to within ± 3 ° of the actual bearing. Data was logged hourly on a SDL 5350 MiniMet and a SDL 5050 DataHog2.

Water levels and peat temperature were measured at each collar at both sites. Water levels were monitored hourly using 12 pressure transducers (Solinst Levelogger Gold, ± 0.3 cm) installed in dipwells 60 cm away from each collar. The dipwells were constructed from 32 mm i.d. polypropylene waste piping (B&Q). The piping was cut to 1.5 m and had holes (6 mm diameter every 2.5 cm on four sides) drilled into the piping to give 15% perforation. A fine mesh was fixed over the holes in the dipwell to protect the holes from clogging up with peat when installed. 30 mm (i.d) cores were dug into the peat to install the dipwells in April 2012. To prevent water level alterations during sampling, duckboards were used when near each of the collars. A barometric pressure transducer (Solinst Barologger Gold, ± 0.1cm) was installed at both sites to compensate for barometric pressure. Water levels were calculated using Eq. 14.

$$A = (L - B) - D \qquad \text{Eq. 14}$$

where A is the actual water level (cm), L is the levelogger total pressure readings (cm), B is barometric pressure (cm) and D is the distance between the top of the chain holding the levelogger in the chamber and the pressure transducer at the bottom of the levelogger (cm; Figure 13). The water level was cross-checked by measuring the water level manually to the top of the dipwell, subtracting the flange height.

Peat temperature was measured hourly at the peat surface (depth of 5 cm; Tiny Tags; manufacturer's stated accuracy of ± 0.4 °C) and at a depth of 90 cm (Solinst Levelogger Gold, manufacturer's stated accuracy of ± 0.05 °C). Subsurface (10 cm below peat surface) temperature was also monitored by the AWS (Skye Instruments MiniMet, manufacturer's stated accuracy of ± 0.2 °C).

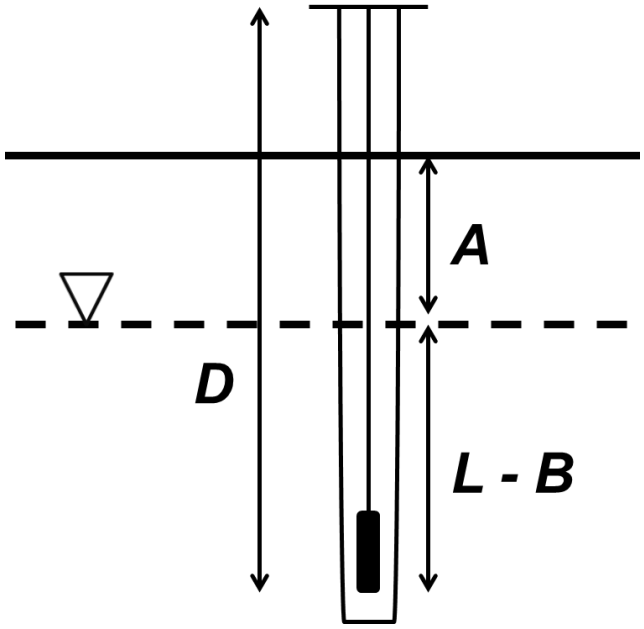


Figure 13 Levelogger diagram. A is the actual water level (cm), L is the levelogger total pressure readings (cm), B is barometric pressure (cm) and D is the distance between the top of the chain holding the levelogger in the chamber and the pressure transducer at the bottom of the levelogger.

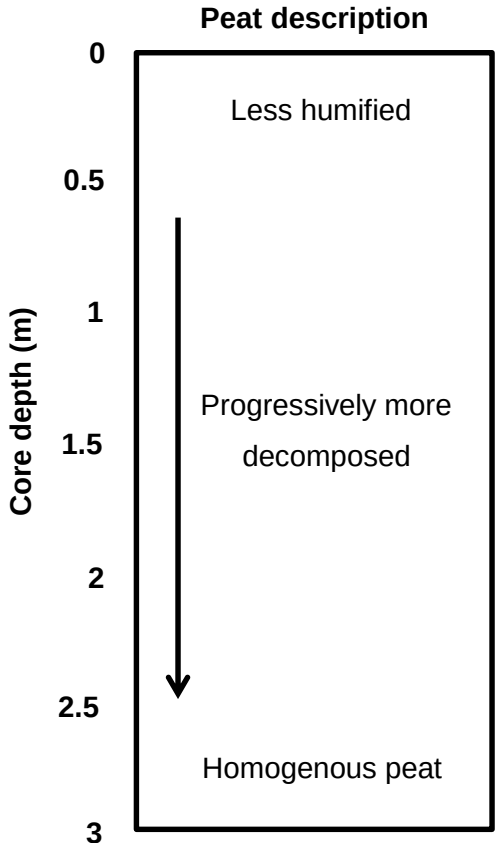
3.2.8 Statistical analysis

All statistical work was undertaken in SPSS/R. Peat core CNPK contents and pH were compared using linear mixed effects models, with depth below the surface as the covariate and core replicates as random effects, using lme function in nlme (Pinheiro et al., 2014). A two-way ANOVA was run on surface peat CNPK contents (< 0.15 m) from March 2013 and June 2013 between Sutton and Strumpshaw Fen, with a Site*Month interaction. Differences in foliar CNPK contents were assessed using a one-way ANOVA. An independent t-test was used to look at differences between dominant plant species at Sutton and Strumpshaw Fen. Correspondence analysis (CA) was undertaken on species composition and abundance data for both sites using the vegan package in R (Oksanen et al., 2013). Independent t-tests were used to ascertain the difference in plant height and aboveground green biomass. ANCOVA was used to ascertain differences in water chemistry for pore-, ditch and river water between sites and rivers, using time as the covariate.

3.3 Results

3.3.1 Peat composition

Differences in peat composition were observed between Sutton (Figure 14; appendix 3) and Strumpshaw Fen (Figure 15; appendix 4) from 3 m cores. Briefly, the peat at Sutton became progressively more decomposed with depth in the profile, whilst Strumpshaw had a dense root mat for ~ 50 cm and then a highly decomposed sloppy peat below.



A gradual change peat in composition and structure throughout the profile, starting with a peat mixture of plant debris, amorphous matter and water (H5), with a dark colour (3 on darkness scale; 7.5 YR, 2.5/2), slight degree of stratification (1) and elasticity (2). Botanical composition consists of roots, stems and rhizomes of herbaceous plants (Th^3) vertically aligned or matted within a growth position.

The peat becomes progressively more decomposed with depth until the peat consists of homogenous peat with roots and fibres distinguishable (H8), with a dark colour (4 on darkness scale; 7.5 YR, 2.5/2), no stratification (0) nor elasticity (0). Botanical composition comprises of humified organics beyond identification.

Figure 14 Sutton Fen peat description, from 3 m cores (*n* = 15 for peat description) taken in June 2013.

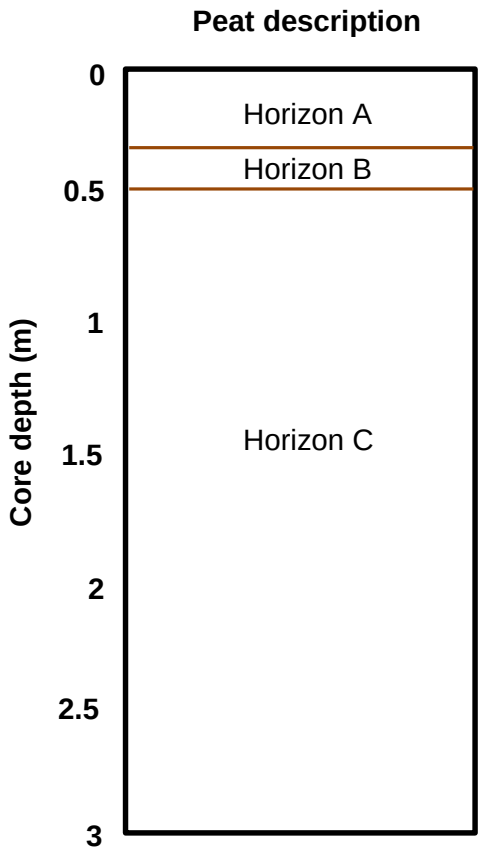


Figure 15 Strumpshaw Fen peat description, from 3 m cores (*n* = 15 for peat description) taken in June 2013.

3.3.2 Peat physicochemistry

Peat physicochemical profiles were established using triplicate 3 m cores extracted from Sutton and Strumpshaw fen in June 2013. Sutton Fen (Figure 16A) had bulk density values ranging from 0.04 to 0.13 g cm^{-3}, which were lower than values reported in the literature for other lowland fens (Boeye et al., 1997, Wassen and Olde Venterink, 2006). Values varied greatly between the triplicate cores and no clear increase or decrease is seen in the average bulk density through the peat profile. Strumpshaw Fen bulk densities ranged from 0.04 to 0.24 g cm^{-3} (Figure 16A), which were within the lower values reported in the literature for lowland fens (Boeye et al., 1997, Wassen and Olde Venterink, 2006). The mean bulk density decreased through the first 120 cm, with two peaks at 20 to 30 cm and 60 to 70 cm, and then increased slightly. A mixed-effects linear model, with site as the independent variable, core depth as a covariate and replicate as a random effect, showed Strumpshaw Fen had significantly greater bulk densities than Sutton Fen (Table 10).

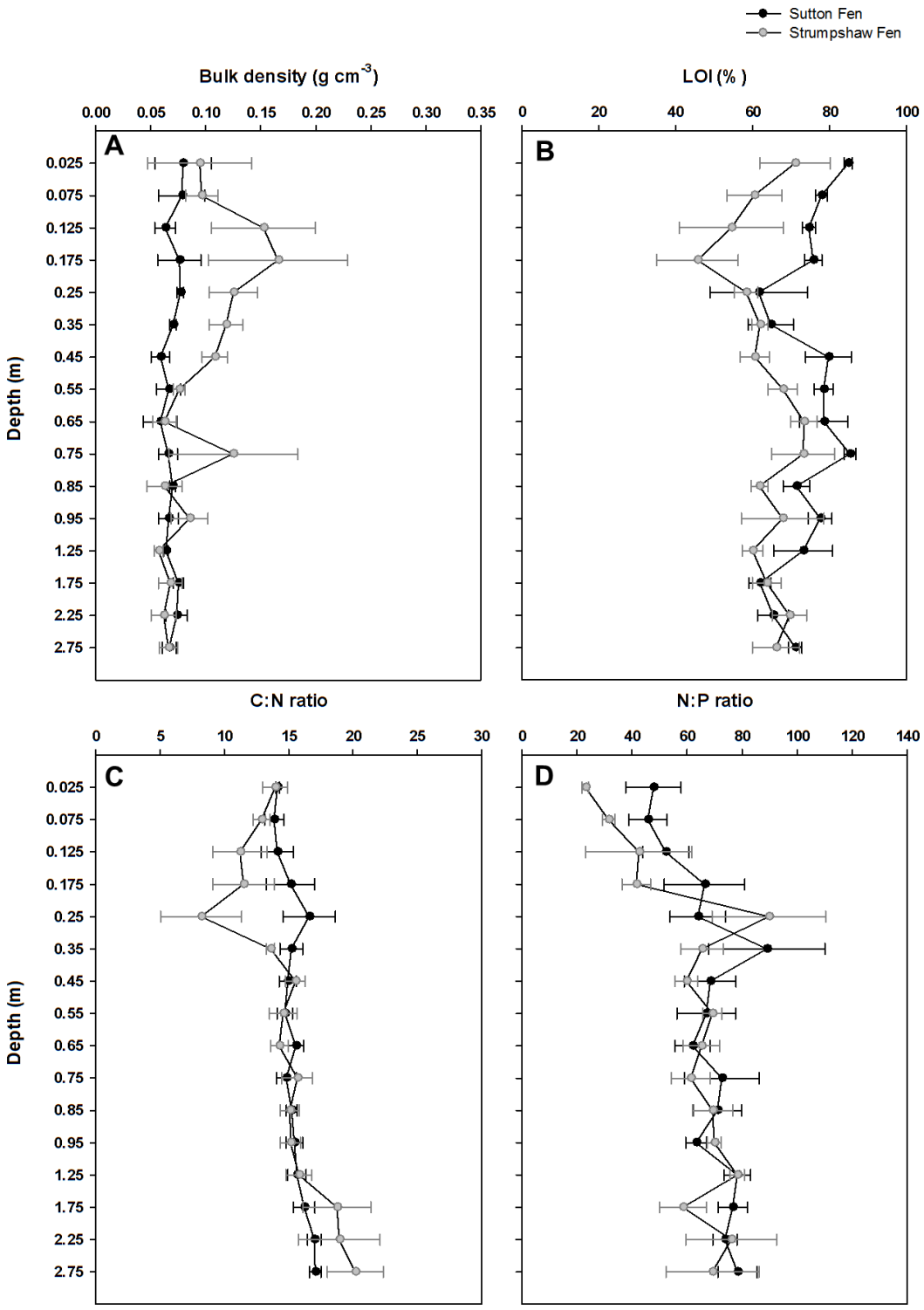


Figure 16 Peat core bulk denisty (A), LOI (B) and C:N (C) and N:P (D) ratios profiles (mean as a solid line and error bars showing ± 1 standard error; full data sets can be found in Appendix 3), from 3 m cores (*n* = 15 for peat description and *n* = 3 for physicochemical profiles) taken in June 2013.

Table 10 Mixed-effects linear model comparing peat core physicochemistry between sites with core depth as a covariate and replicates as random effects. ** signifies a *p*-value <0.001, whilst * represents a *p*-value of <0.05.

	Independent variable (Site)		Covariate (Depth)	
	F value	*p*-value	F value	*p*-value
C	2.890	0.093	23.824	<0.001**
N	0.008	0.928	2.517	0.116
P	2.377	0.127	21.754	<0.001**
K	46.566	<0.001**	45.347	<0.001**
C:N	0.918	0.341	44.015	<0.001**
N:P	3.114	0.081	14.368	<0.001**
Bulk density	9.226	0.003*	6.232	0.003*
LOI	22.154	<0.001**	0.333	0.565
pH	9.61	0.003*	13.08	<0.001**
When the models were run including the interaction terms between site and month, they were not significant.				

Organic matter content (by LOI) for Sutton Fen (Figure 16B) ranged from 38 to 87 %, which were amongst the higher values reported in the literature for lowland fens (37 – 82 %) (Boeye et al., 1997, Wassen and Olde Venterink, 2006). There was a rapid decrease in mean LOI from the surface to 30 cm, before an increase again. From 50 cm, there was a gradual decrease in average LOI through the profile until 150 to 200 cm, where it then starts to increase again. Strumpshaw Fen's LOI percentages (Figure 16B) ranged from 30 to 89 % and were within the higher values reported in the literature for lowland fens (Boeye et al., 1997, Wassen and Olde Venterink, 2006). As for bulk density, a spike occurs between 20 to 30 cm below the surface. LOI was significantly greater at Sutton Fen than at Strumpshaw Fen (Table 10).

Core CNPK contents are shown in Figure17. C, P and K contents were all within the literature values for lowland fens (Boeye et al., 1997, Syed et al., 2006, Wassen and Olde Venterink, 2006). C contents for Sutton and Stumpshaw ranged from 199 to 600 and 142 to 709 g kg^{-1}, respectively. Average core C contents were 440 and 408 for Sutton and Strumpshaw respectively. N contents ranged from 10 to 39 and 8.1 to 212 g kg^{-1} and mean contents of 29 and 34 g kg^{-1} for Sutton and Strumpshaw respectively. Interestingly, the top 15 cm of the average core N content for Sutton Fen was greater than Strumpshaw

(approximately 30 g kg^{-1} compared to 24 to 27 g kg^{-1}), yet Strumpshaw had a higher core profile average (34 g kg^{-1} instead of 29 g kg^{-1}). N contents were higher than those stated in the literature (Boeye et al., 1997, Syed et al., 2006, Wassen and Olde Venterink, 2006). P and K contents at Sutton ranged from 0.2 to 0.9 g kg^{-1} and 0 to 0.6 g kg^{-1}, respectively. Strumpshaw P and K contents ranged from 0.3 to 1.3 g kg^{-1} and 0.1 to 1, respectively. Only K contents were found to be significantly greater at Strumpshaw Fen than at Sutton Fen (Table 10).

C:N ratios (Figure 16C) through the core profiles at Sutton Fen ranged from 12 to 20, which are within the literature values for fens (Koerselman et al., 1993, Kasimir-Klemedtsson et al., 1997). The mean C:N ratio gradually increased throughout the profile, with a small spike between 30 to 40 cm. Additionally, the mean N:P ratio (Figure 16D) gradually increased through the profile and has a spike between 30 and 40 cm. N:P ratios ranged from 33 to 126. At Strumpshaw Fen, C:N ratios were within the literature values (Koerselman et al., 1993, Kasimir-Klemedtsson et al., 1997), ranging from 3.3 to 25. Mean C:N ratio followed an increasing pattern throughout the profile until the last 50 cm, where there was a sudden decrease, caused due to a high N content (Figure 17; 212 g kg^{-1}) in one of the cores. This also affected the average N:P ratio (Figure 16D), which followed a similar pattern to the C:N ratio, with peaks between 20 to 30 cm and 60 to 70 cm. The N:P ratios ranged from 21 to 523. Peat core pH values are shown in Figure 18 and ranged between 6.2 and 6.8. The peat became more acidic with depth at Strumpshaw Fen; however, this pattern was not observed at Sutton Fen, where an increase in pH was observed from 0 to 20 cm and then the pH remained similar throughout the rest of the profile. There was a significant difference in pH between sites (Table 10).

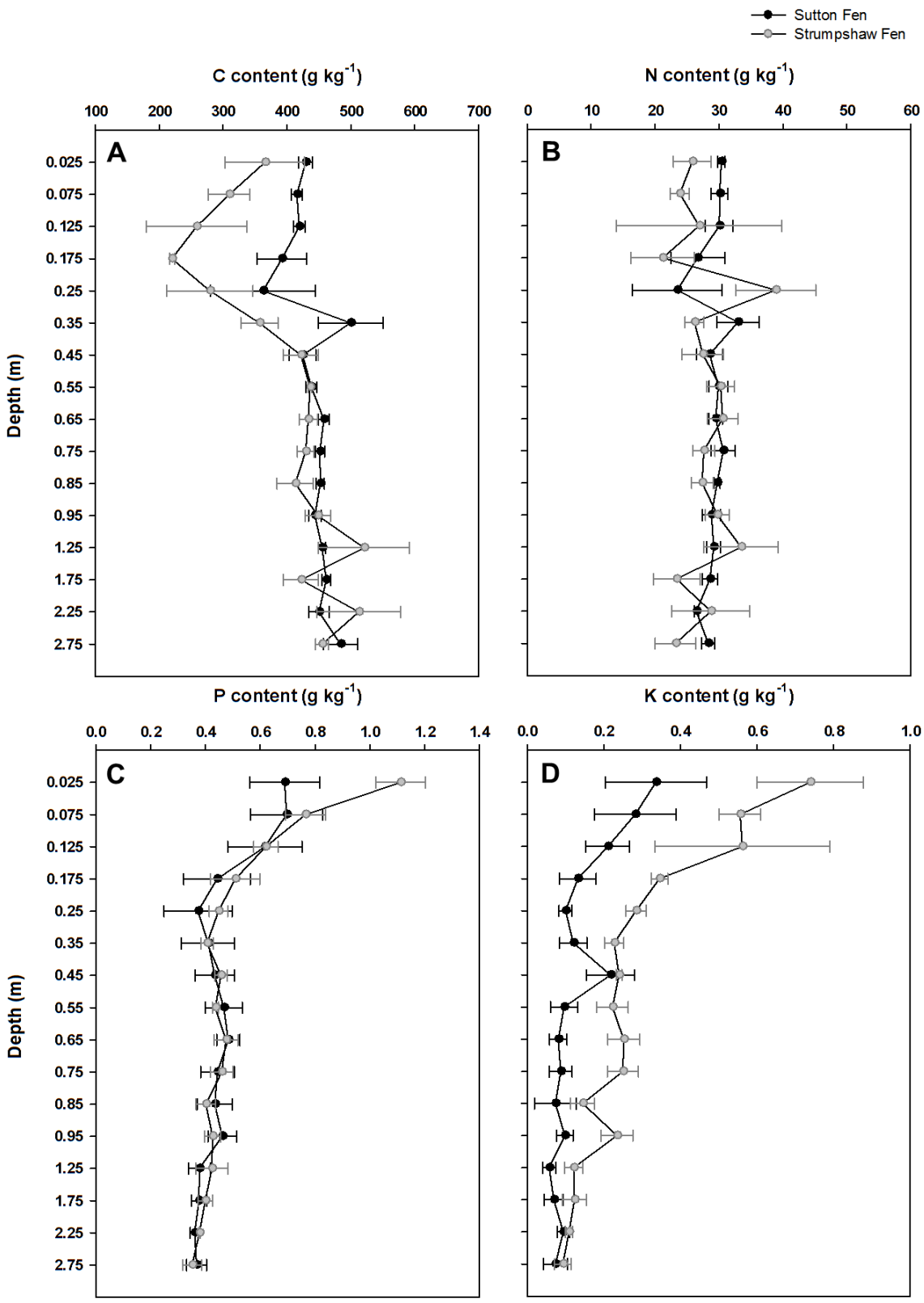


Figure 17 Average core (*n* = 3; solid circles) C (A), N (B), P (C) and K (D) contents for Sutton and Strumpshaw Fen in June 2013. Error bars represent ± 1 standard error.

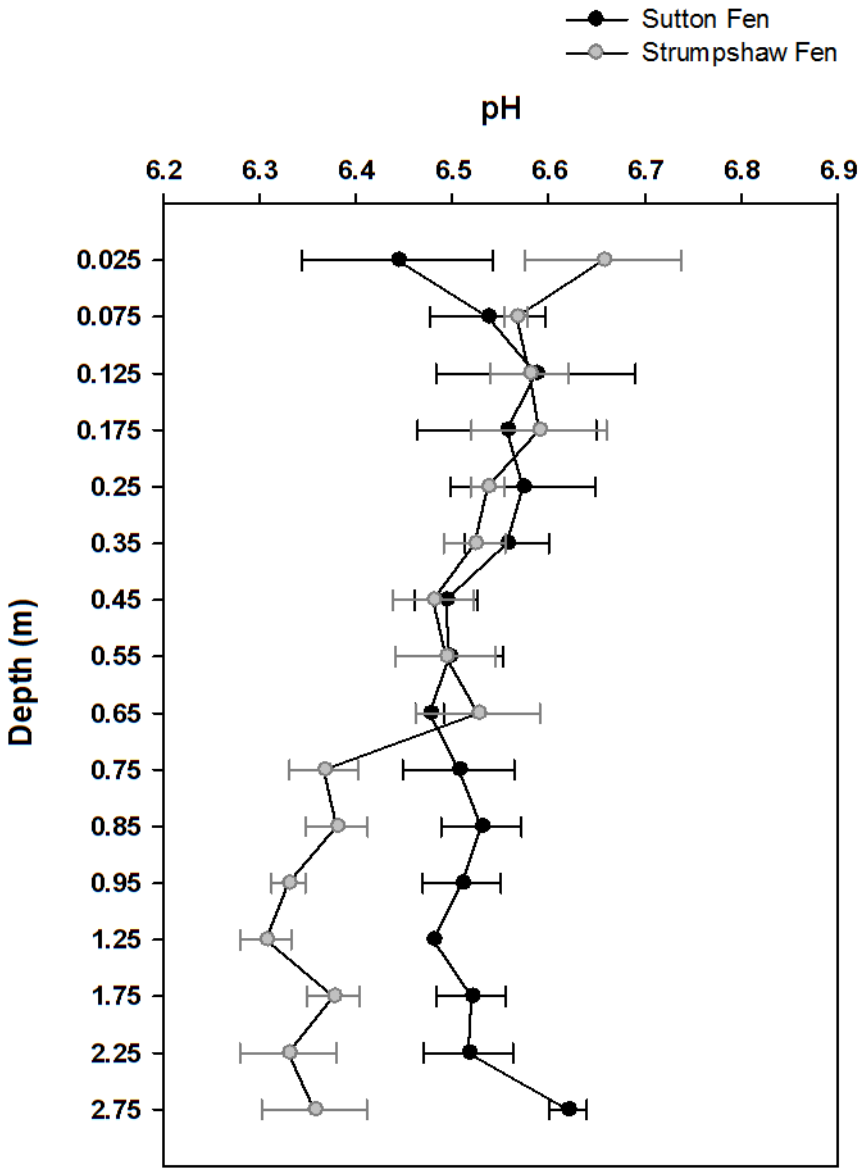


Figure 18 Core pH profiles for Sutton and Strumpshaw Fen from 3 m cores (*n* = 3) taken in June 2013. Triplicate mean shown as a solid line with error bars representing ± 1 standard error; full data sets can be found in Appendix 4.

In March 2013, surface peat samples (< 0.15 m below peat surface) were taken from Sutton and Strumpshaw Fen for CNPK analysis (Table 11) to provide surface nutrient contents to inform experiments described in chapter 6. Data has been included in this chapter as a two-way ANOVA revealed a significant difference in surface peat N contents were significantly different between Sutton and Strumpshaw Fen and between March 2013 and June 2013 (Table 11). N contents were significantly greater at Strumpshaw (28 ± 0.4 g kg^{-1}) than Sutton (18 ± 0.9 g kg^{-1}) in March 2013, whereas in June 2013 N contents were significantly greater at Sutton (30 ± 0.2 g kg^{-1}) than Strumpshaw (26 ± 0.9

g kg^{-1}). A significant difference in surface peat P and K contents was also observed between sites (Table 11).

Table 11 Average surface peat (15 cm) C, N, P and K contents [± 1 S.E.] at Sutton (*n* = 5) and Strumpshaw Fen (*n* = 5) from March and June 2013 and two-way ANOVA with Site*Month interaction values for peat nutrient analysis for March 2013 data. Significant differences between sites are shown using * (<0.05).

Element	March 2013 Site		June 2013 Site	
	Sutton	**Strumpshaw**	**Sutton**	**Strumpshaw**
C (g kg^{-1})	373 [± 22]	386 [± 5.0]	421 [± 4.1]	345 [± 18]
N (g kg^{-1})	18 [± 0.9]	28 [± 0.4]	30 [± 0.7]	26 [± 0.9]
P (g kg^{-1})	0.4 [± 0.01]	0.9 [± 0.02]	0.7 [± 0.03]	0.8 [± 0.2]
K (g kg^{-1})	0.3 [± 0.02]	0.3 [± 0.01]	0.3 [± 0.03]	0.6 [± 0.03]

		Site		**Month**		**Site*Month**	
	df	**F-value**	***p*-value**	**F-value**	***p*-value**	**F-value**	***p*-value**
C	1,20	1.872	0.186	0.00	0.995	0.936	0.345
N	1,20	4.920	0.038*	2.519	0.128	24.483	<0.001**
P	1,24	11.051	0.002*	3.823	0.062	1.688	0.206
K	1,24	12.456	<0.001**	2.071	0.163	6.310	0.019*

3.3.3 Plant species and abundance

Plant species abundance and composition was assessed using the Domin scale (Currall, 1987) in September 2012 (Table 12) by a plant ecologist (Dr Andrew Skinner) from the RSPB (full dataset in appendix 1 and 2). Species observed are typical of a reed fen, with Sutton Fen classified as S24 under the NVC classification (*P. australis-P. palustre* fen) and Strumpshaw Fen classified as S25 (*P. australis-E. cannabinum* fen) (Broads Authority, 2010). Both sites are dominated by *P. australis*, although Strumpshaw Fen has a greater abundance than Sutton Fen (values of 7-8 compared with 1-5 at Sutton). A number of other species are common throughout both sites, such as *Carex spp.* and *G. palustre.* Sutton Fen showed a greater number of total species present in the collars (34 species compared to 31 at Strumpshaw).

Table 12 Herbaceous plants and bryophyte composition and abundance at Sutton and Strumpshaw Fen (Domin scale – 1 to 9) measured in September 2012 at each collar (n = 6; full data set in Appendix 3 and 4).

Species	Sutton Fen						Strumpshaw Fen					
	1	2	3	4	5	6	1	2	3	4	5	6
Agrostis stolonifera L. (1753)	1	1		1	1			6	1		2	7
Berula erecta (Huds.) Coville (1893)	1		3	3		3	1	6				
Calamagrostis canescens L. (Weber) Roth (1789)			5	4	2		8		8		3	
Cardamine spp.			1		1	1		1	1	2	1	
Carex acutiformis Ehrh. (1789)								1				
Carex appropinquata Schumach. (1801)											1	
Carex elata All. (1785)					6							
Carex pseudocyperus L. (1753)	1		4	2		6						
Carex riparia Curtis (1783)								4				
Carex spp.	1											
Calystegia sepium (L.) R. Br. (1810)									2			
Cladium mariscus (L.) Pohl (1809)		5	1	1	5							
Cirsium palustre (L.) Coss. ex Scop. (1772)						1						
Epilobium palustre L. (1753)	1			1							4	
Epilobium parviflorum Schreb. (1771)				1			1					
Eupatorium cannabinum L. (1753)				1	1	1	5		5	1	5	1
Galium palustre L. (1753)	4			2	2	2	1	4	5	3	7	1
Holcus lanatus L. (1753)						4						
Hydrocotyle vulgaris L. (1753)	2											
Iris pseudacorus L. (1753)							1					
Juncus articulatus L. (1753)			1									
Juncus subnodulosus Schrank (1789)	4	3	1	4	2						1	
Lathyrus palustris L. (1753)							2	5	1		5	
Lemna minor L. (1753)										5		4
Lychnis flos-cuculi L. (1753)							6					
Lycopus europaeus L. (1753)				1		1				1		1
Lysimachia nummularia L. (1753)											1	
Lysimachia vulgaris L. (1753)	2	2	1	4	2	3	2		4		3	
Lythrum salicaria L. (1753)	2		1	1				2				
Mentha aquatica L. (1753)	3		3	3	3	6		5			1	

Myosotis laxa Lehm. (1818)	1					1						
Oenanthe fistulosa L. (1753)	1	1	1	1	1	1						
Pedicularis palustris L. (1753)	4	2		3	1							
Peucedanum palustre (L.) Moench (1794)		1					1	1	3		3	
Phalaris arundinacea L. (1753)							4					
Phragmites australis (Cav.) Trin. ex Steud. (1841)	2	4	4	4	1	5	8	7	8	8	7	7
Potamogeton coloratus Hornem. (1813)						4						
Ranunculus lingua L. (1753)		1										2
Salix spp.			4	1								
Scutellaria galericulata L. (1753)			1									
Sium latifolium L. (1753)	1	2			2							
Solanum dulcamara L. (1753)									1		1	
Sonchus palustris L. (1753)											3	
Stellaria palustris Ehrh. ex Retz. (1795)	1			1			1		1		1	
Thelypteris palustris Schott (1834)	8	6	6	7	8				9			
Typha latifolia L. (1753)		1			1							2
Bryophytes	9		6	6	1	2		5	8	8	5	

Mann Whitney-U analyses (data could not be normalised) on dominant plant species within collars showed that there are many species that are of similar abundance at both sites (Table 13; $p > 0.05$). There are a number of the dominant plant species that differ in abundance between sites, including *P. australis*, *C. pseudocyperus*, *J. subnodulosus* and *L. palustris* (Table 13). The difference in *P. australis* abundance between Sutton and Strumpshaw, along with the difference in vegetation height, can be used as a proxy for differing nutrient status between sites, as the species is more abundant and has taller shoots with higher nutrient availability (at Strumpshaw Fen) (Gorham and Pearsall, 1956, Allen and Pearsall, 1963, Engloner, 2009).

Table 13 A comparison of plant species dominance (% cover, transformed from Domin scale) between Sutton and Strumpshaw fens using a Mann Whitney-U test. Significant difference between sites shown using * (< 0.05) and ** (< 0.001).

	U-value	*P*-value
Calamagrostis canescens (Weber) Roth (1789)	16	0.669
Carex acutiformis Ehrh. (1789)	15	0.317
Carex appropiriquita Schumach. (1801)	15	0.317
Carex elata All. (1785)	15	0.317
Carex pseudocyperus L. (1753)	6	0.022*
Carex riparia Curtis (1783)	15	0.317
Carex spp.	15	0.317
Carex spp. Total	7	0.067
Cladium mariscus (L.) Pohl (1809)	6	0.022*
Eupatorium cannabinum L. (1753)	8	0.073
Galium palustre L. (1753)	10	0.168
Juncus subnodulosus Schrank (1789)	4	0.016*
Lathyrus palustris L. (1753)	6	0.022*
Lemna minor L. (1753)	12	0.140
Lysimachia vulgaris L. (1753)	13	0.365
Mentha aquatica L. (1753)	8	0.091
Phalaris arundinacea L. (1753)	15	0.317
Phragmites australis (Cav.) Trin. ex Steud. (1841)	0	0.003**
Thelypteris palustris Schott (1834)	9	0.103

Dominant plant species are not necessarily a key indicator of differences in vegetation between sites. CA showed a difference in vegetation composition and abundance between sites (Figure 19A), with a complete separation in site by species assemblage. Within-site variation was less at Strumpshaw than Sutton Fen, with most of the collars clustered closely together, showing a similarity in species and abundance. The dominance of *P. australis, C. canescens* and *E. cannabinum* at the site results in the clustering together of values and a positive CA1 value (Figure 19A). Sutton Fen was less densely clustered, showing the variance in species composition and abundance at the site (Figure 19B). The occurrence of *Potamogeton coloratus* Hornem. (1813) in collar 6 at Sutton Fen caused a negative value on CA2, whilst the occurrence of *C. elata* in collar 5 and *C. mariscus* in collar 1 caused the greater positive values on CA2 for the two collars at Sutton Fen.

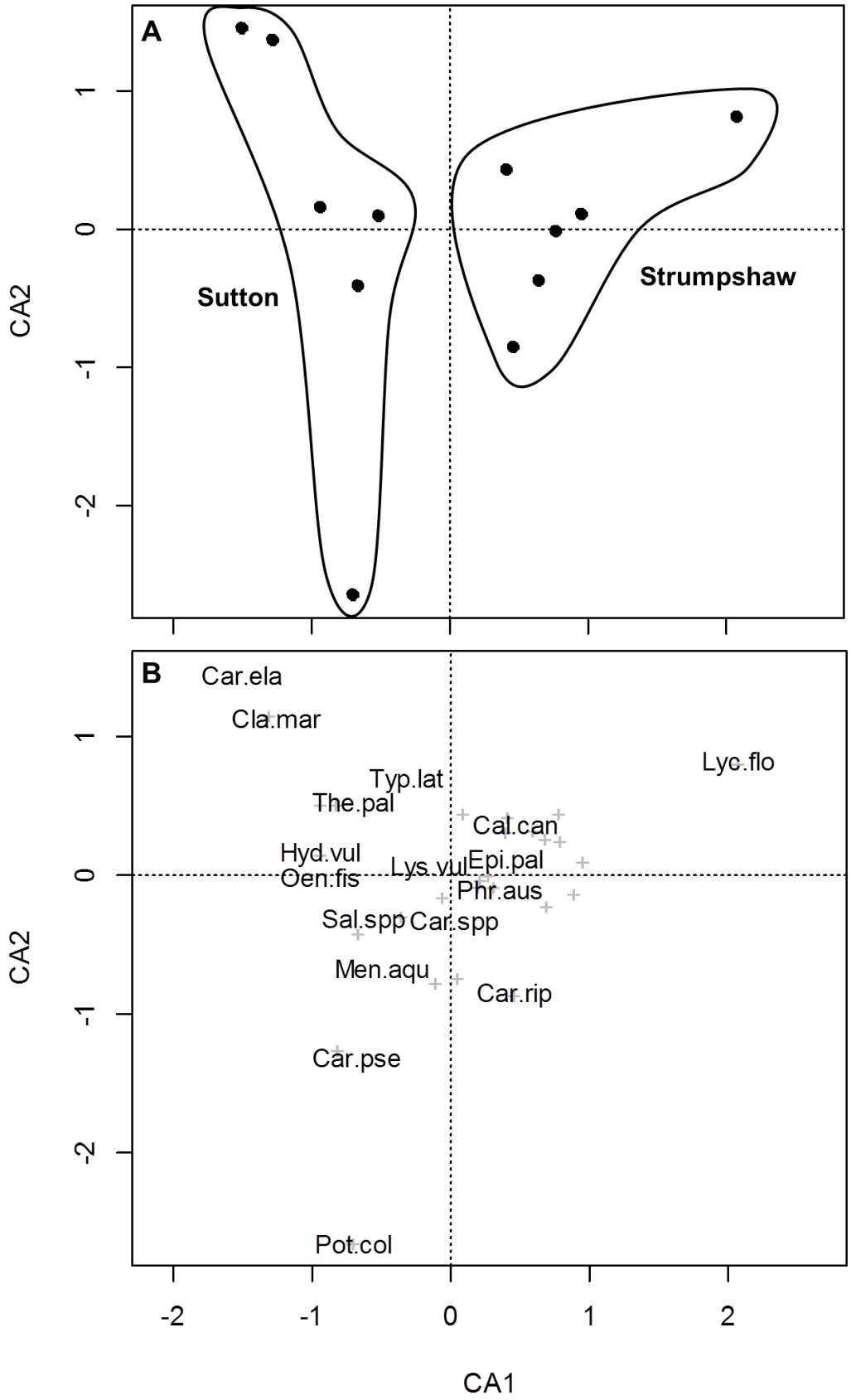


Figure 19 Correspondence analysis (CA) scatter diagram of cover estimation of vegetation (A) between sites. CA scatter diagram of the plant species (B) at both sites. Species names and results from CA are shown in Appendix 5.

3.3.4 Plant height and above-ground biomass

Average vegetation height in each collar (n = 6 per site; Figure 20A) was measured at the same time as species identification by Dr Andrew Skinner from RSPB in September 2012. This data was used as a proxy for differences in nutrient status as nutrient limitation can restrict plant growth (Koerselman and Meuleman, 1996). Mean heights [± 1 S.E.] for Sutton and Strumpshaw Fen were 57 [± 5.1] cm and 107 [± 7.8] cm, respectively. Sutton had a maximum height of 72 cm and a minimum of 44 cm, whilst Strumpshaw had 127 cm and 79 cm, respectively. A t-test showed that collar vegetation height was significantly greater at Strumpshaw Fen than at Sutton Fen (Figure 20).

Above-ground green biomass from September 2013 was used as a proxy for productivity at both sites (Figure 20B). Mean [± 1 S.E.] above-ground green biomass for Sutton Fen was 435 [± 42] g m^{-2} in September 2013, with a minimum of 203 g m^{-2} and a maximum of 677 g m^{-2}. Strumpshaw had a greater mean above-ground green biomass of 1578 [± 169] g m^{-2}, with a minimum of 825 g m^{-2} and a maximum of 2305 g m^{-2}. Above-ground green biomass results are within the literature values for both the Norfolk Broads (Wheeler and Giller, 1982) and other lowland fens (Boeye et al., 1997, Wassen and Olde Venterink, 2006). An independent t-test showed that there was a statistically significant difference between sites for productivity (Figure 20), indicating a potential difference in nutrient status between sites as vegetation within the sampling site was taken from areas cut at the same time.

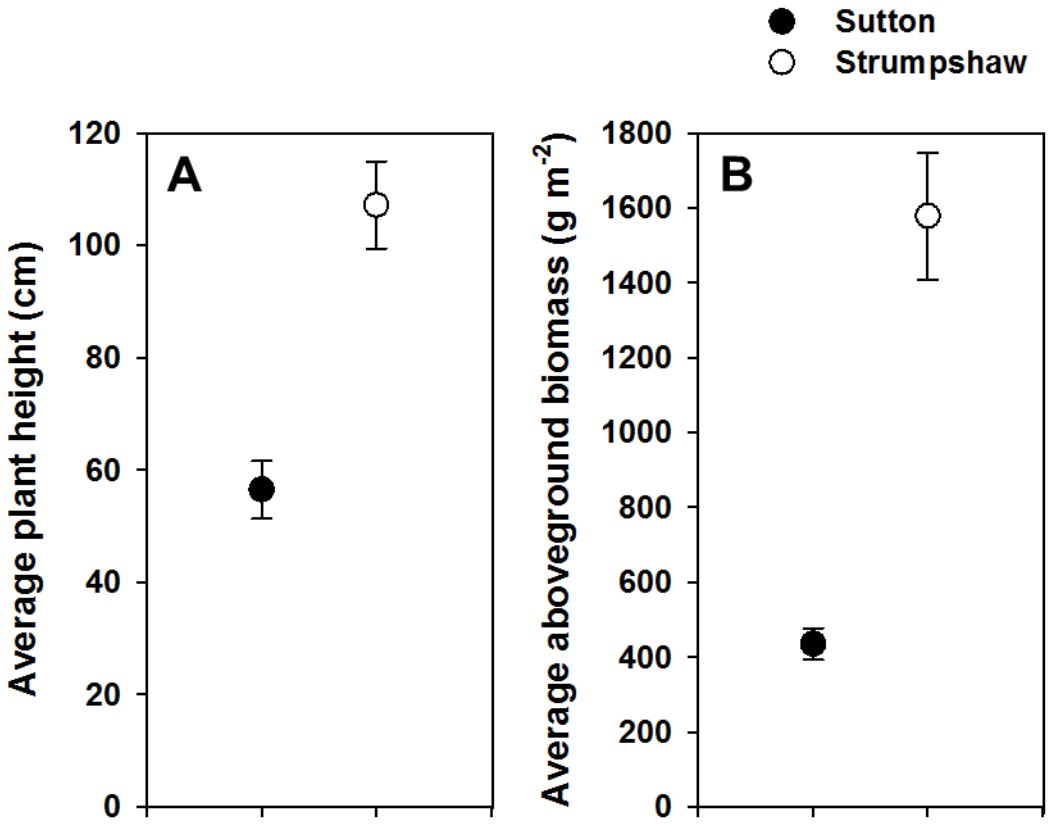


Figure 20 Average collar vegetation height (A) for Sutton (*n* = 6) and Strumpshaw Fen (*n* = 6) in September 2012 and above-ground biomass (B) in September 2013. Error bars represent ± 1 standard error. Independent t-tests showed a significant difference in average vegetation height (t_{10} = -5.438, p < 0.001) and aboveground green biomass ($t_{10.129}$ = -6.5585; p < 0.001).

3.3.5 Foliar nutrient contents

Foliar nutrient content of leaves collected at peak biomass on 12th September 2012 are shown in Figure 21. Mean foliar nutrient contents revealed significant differences for N and P (Table 14) between sites, with greater mean [± 1 S.E.] contents at Strumpshaw (22 [± 1.5] g kg^{-1} and 2 [± 0.2], respectively) than Sutton (16 [± 1.5] g kg^{-1} and 1.1 [± 0.1], respectively). Mean foliar C and K (Figure 20) contents ± 1 standard error were 427 ± 2.8 g kg^{-1} and 11 ± 1.2 g kg^{-1} for Sutton and 420 ± 4.6 g kg^{-1} and 10 ± 1.3 g kg^{-1} for Strumpshaw, respectively. All foliar CNPK contents were within high end of the literature values (Figure 22) (Allen and Pearsall, 1963, de Mars et al., 1996, Olde Venterink et al., 2001, Olde Venterink et al., 2002, Olde Venterink et al., 2003).

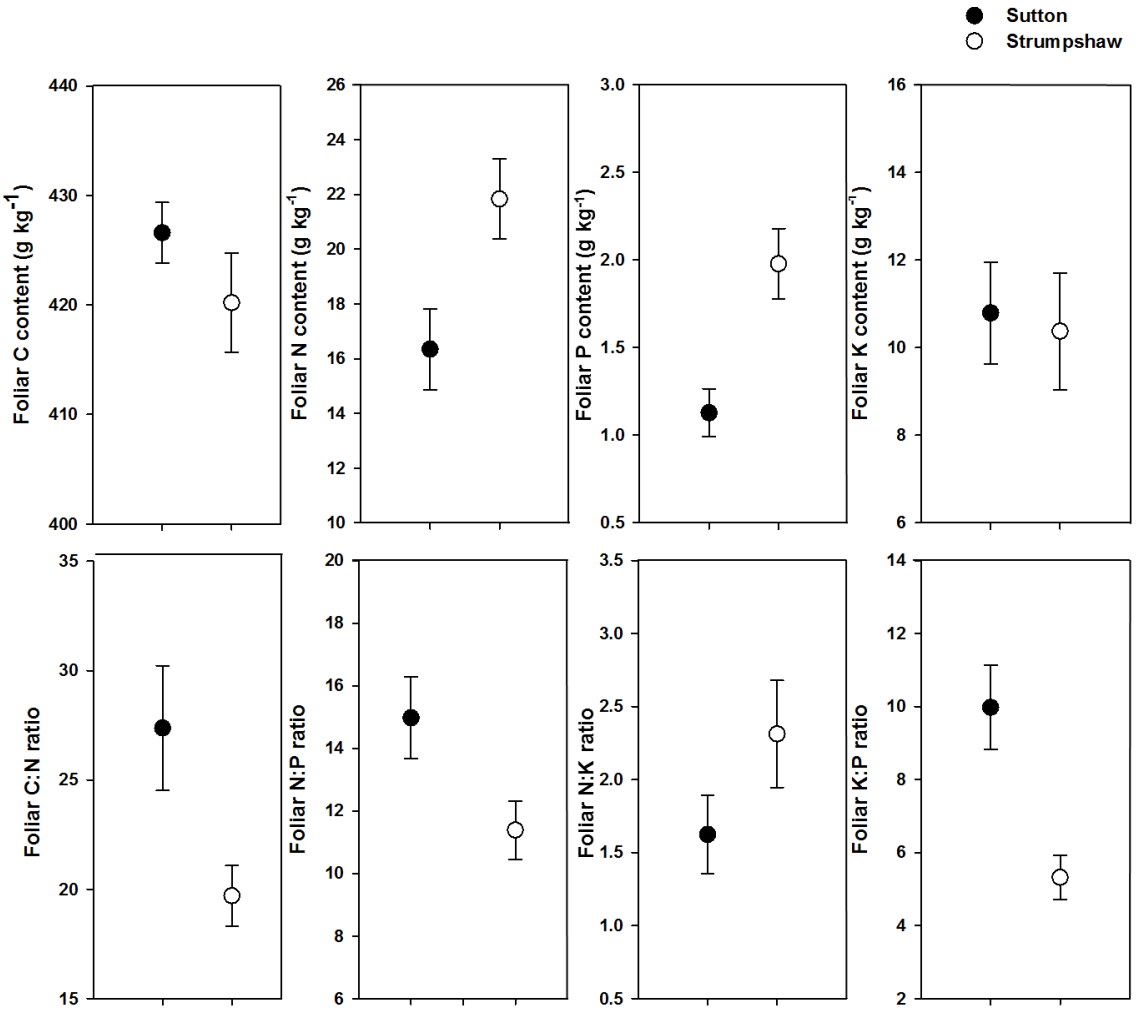
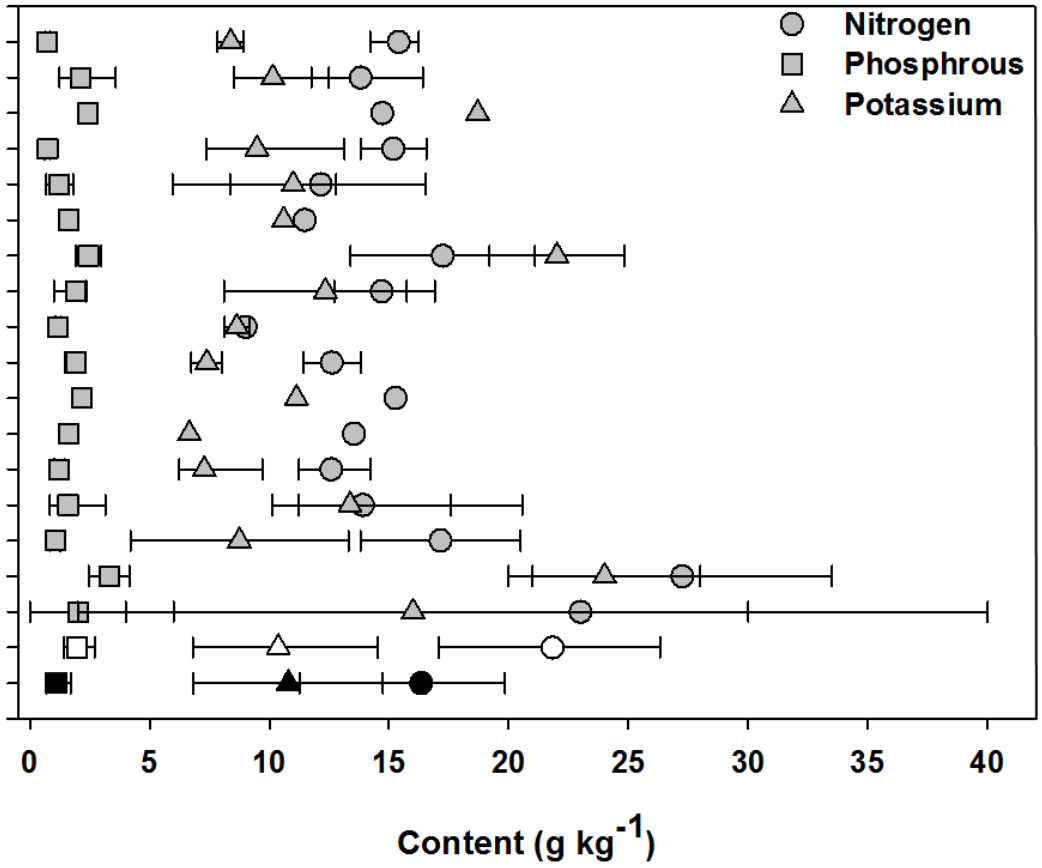


Figure 21 Mean collar vegetation C, N, P and K contents (*n* = 6) and N:P, N:K, K:P and C:N ratios from vegetation collected in September 2012. Error bars represent ± 1 standard error.

Table 14 Independent t-test results for foliar CNPK contents, C:N, N:P, K:P and N:K ratios between sites. ** signifies a *p*-value <0.001, whilst * represents a *p*-value of <0.05.

	df	t-value	*p*-value
C	8.247	1.1987	0.264
N	9.999	-2.6383	0.025*
P	8.779	-3.5043	0.007*
K	9.871	0.2362	0.818
C:N	7.248	2.4234	0.045*
N:P	9.044	2.2265	0.053*
K:P	7.503	2.5828	0.008*
N:K	9.195	-1.5202	0.162

Foliar nutrient ratios (Figure 23) calculated from foliar CNPK contents showed that collars 2, 4 and 5 at Sutton Fen and collar 4 at Strumpshaw Fen were P limited (N:P ratios of 17, 17, 19 and 15, respectively), whilst the remaining collars at Sutton (*n* = 3) and Strumpshaw (*n* = 1) were all N limited (Figure 23). N:P ratios ranged from 12 to 19 and 8.4 to 15 at Sutton and Strumpshaw, respectively. N:K ratios ranged from 1.0 to 2.8 and 1.4 to 3.6 for Sutton and Strumpshaw, respectively. Sutton K:P ratios ranged from 6.1 to 13, whilst Strumpshaw had a minimum of 4 and a maximum of 7.2. Sutton and Strumpshaw had C:N minima and maxima of 22 to 38 and 16 to 25, respectively. C:N, N:P and K:P ratios were significantly greater at Sutton than at Strumpshaw Fen (Table 14). Ratios are within a similar distribution to those in the lowland fen literature (Figure 24).



Site	Peatland type	Country	Study
TA10	PF	P	Wassen *et al.* (1990)
TA14	PF	P	Wassen *et al.* (1990)
TA	RF	P	Wassen *et al.* (1990)
ZW10	PF	B	Olde Venterink *et al.* (2001)
TA03	RF	P	Wassen *et al.* (1990)
TC	RF	P	Wassen *et al.* (1990)
UZ13	RF	NL	Olde Venterink *et al.* (2003)
ZW11	RF	B	Olde Venterink *et al.* (2001)
UZ	RF	NL	Olde Venterink *et al.* (2001)
RV2	RF	NL	Olde Venterink *et al.* (2003)
ZW7	FM	B	Olde Venterink *et al.* (2001)
RV1	FM	NL	Olde Venterink *et al.* (2001)
BB	FM	NL	Olde Venterink *et al.* (2001)
TA21	FF	P	Wassen *et al.* (1990)
Jergznia	FF	P	Boorman and Fuller (1981)
Norfolk Broads	FF	UK	Boorman and Fuller (1981)
Norfolk Broads	FF	UK	Mason and Bryant (1975)
Strumpshaw Fen	FF	UK	
Sutton Fen	FF	UK	

FF = Floodplain fen, FM = Fen meadow, RF = Rich Fen and PF = Poor Fen

Figure 22 Comparison of foliar NPK contents with values reported in the literature. Points show mean values, whilst error bars shown minima and maxima.

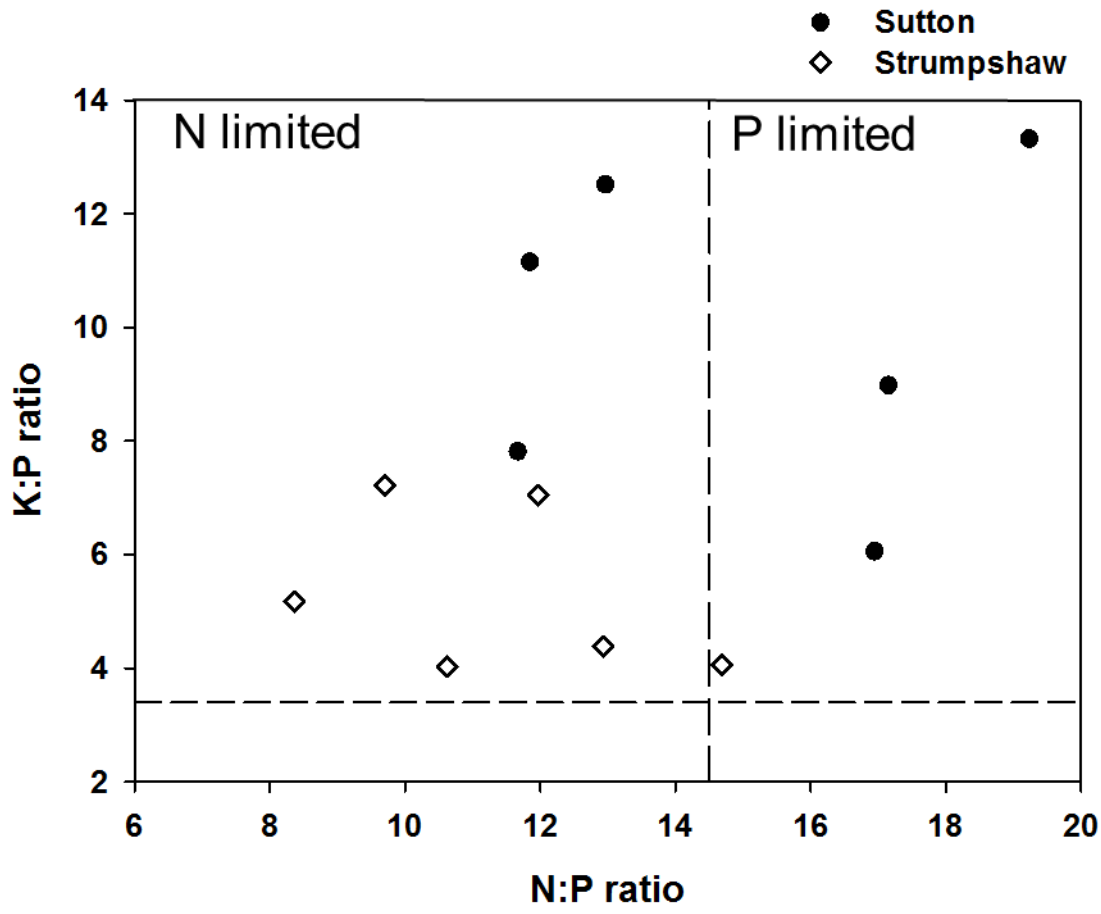
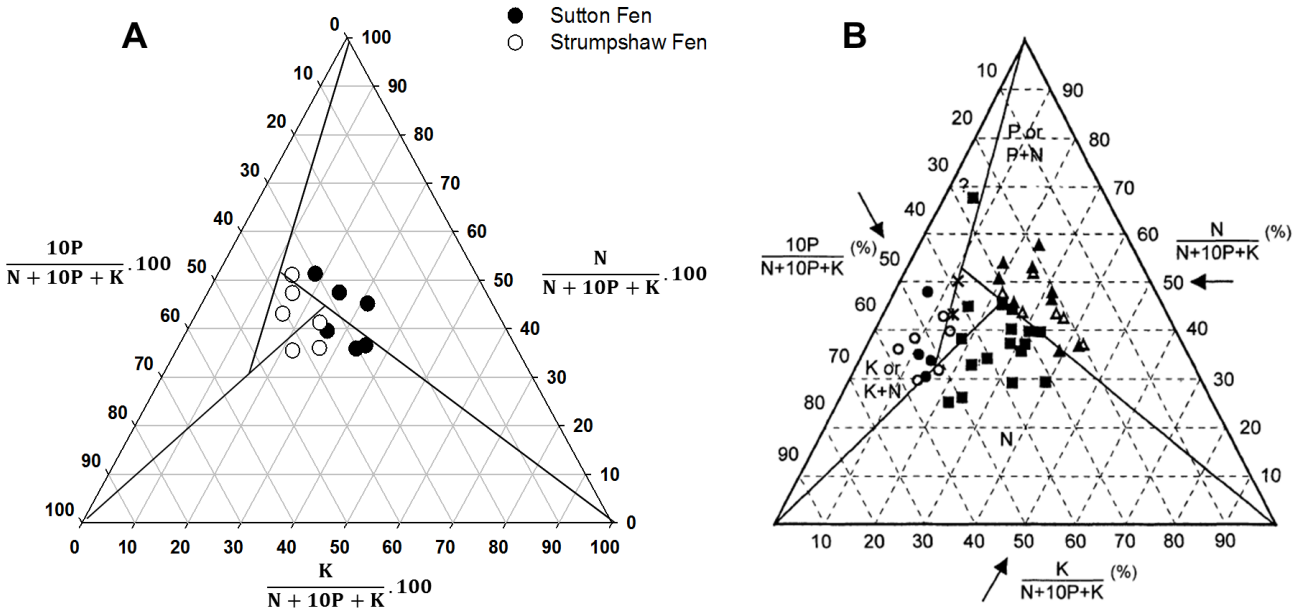


Figure 23 Collar vegetation nutrient limitation using N:P and K:P ratios for Sutton and Strumpshaw Fen. Lines showing limitation for N:P (14.5) and K:P (3.4) are derived from Olde Venterink et al. (2003) and Gusewell (2004).



Source: Olde Venerink et al. (2003, p. 2194)

Figure 24 Ternary plot showing the relationship between foliar N:P:K contents and nutrient limitation in Sutton and Strumpshaw Fen (A) and 44 European wetlands (B).

3.3.6 Pore-, ditch and river water chemistry

Porewater chemistry parameters are shown in Figure 25 and 26. Dissolved CO_2 and CH_4 porewater concentrations followed a seasonal pattern over the 16 month sampling period (Figure 25; Table 15). Dissolved CO_2 concentrations were significantly greater at Sutton Fen (Table 15 and 16) than at Strumpshaw Fen. Porewater DOC concentrations also showed a seasonal pattern, with concentrations significantly greater at Sutton Fen than at Strumpshaw Fen (Figure 25C; Table 15 and 16). Unlike DOC, DIC did not follow a seasonal pattern (Figure 25D and Table 15). Both Sutton and Strumpshaw Fen had relatively neutral porewater, with a pH ranging between 6 and 8 (Figure 25E; Table 15). Strumpshaw Fen generally had a higher electrical conductivity (EC; Figure 25F; Table 15 and 16) than at Sutton Fen and followed a seasonal pattern. Porewater NO_3^-, SRP, Cl^- and SO_4^{2-} concentrations were significantly greater at Strumpshaw Fen (Figure 26; Table 15 and 16) than at Sutton Fen. Porewater NH_4^+ and Fe^{2+} concentrations were significantly greater at Sutton Fen than at Strumpshaw Fen (Figure 26; Table 15 and 16).

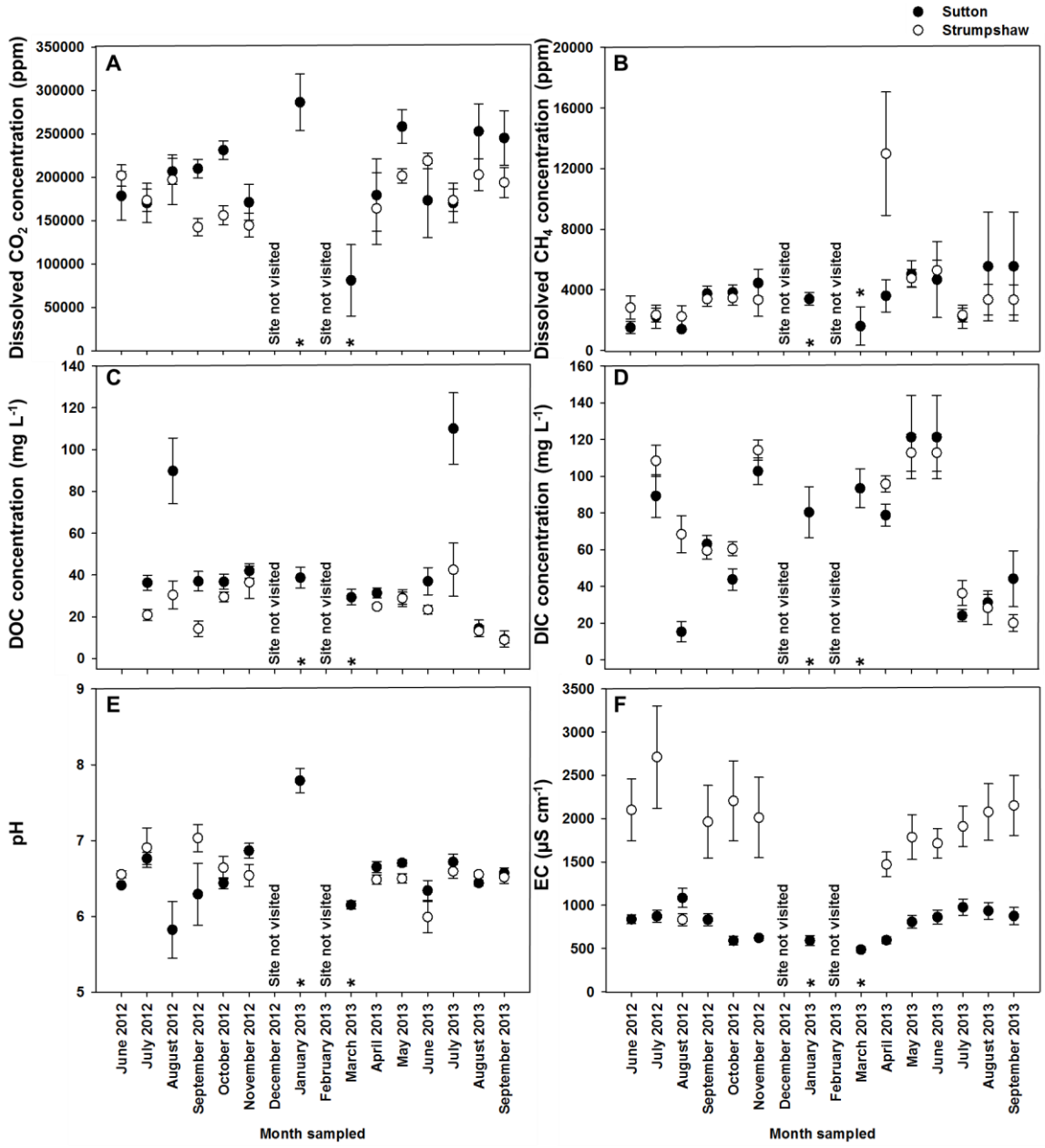


Figure 25 Monthly porewater dissolved CO_2 (A), dissolved CH_4 (B), DOC (C), DIC (D), pH (E) and electrical conductivity (EC; F) from 18th June 2012 to 6th September 2013 at Sutton and Strumpshaw Fen. Strumpshaw Fen was not visited in January 2013. Points represent mean values and error bars denote ± 1 standard error. * indicate when only Sutton Fen was sampled.

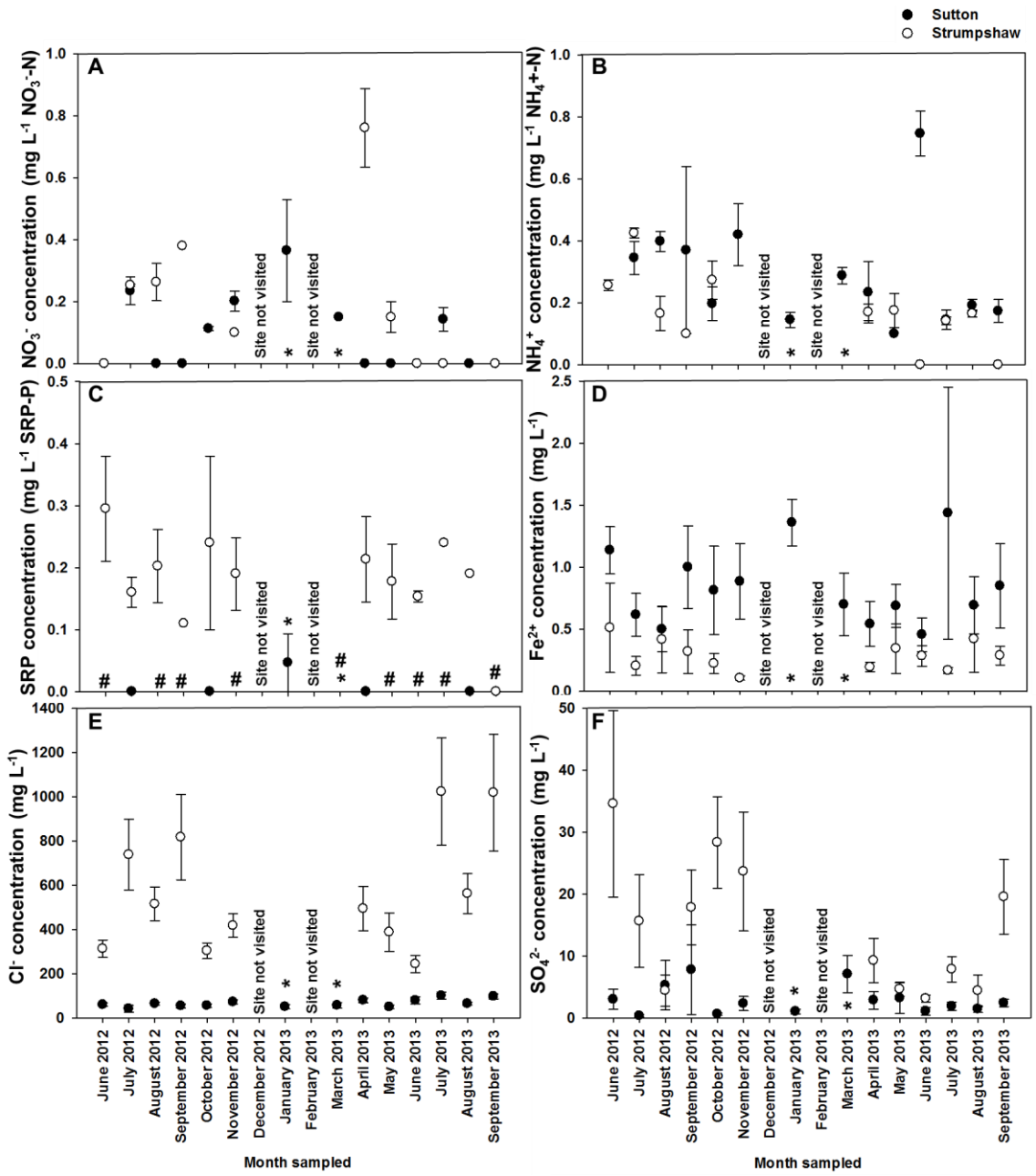


Figure 26 Monthly porewater NO_3^- (mg L^{-1} NO_3^--N; A), NH_4^+ (mg L^{-1} NH_4^+-N; B), SRP (mg L^{-1} SRP-P; C), Fe^{2+} (mg L^{-1}; D), Cl^- (mg L^{-1}; E) and SO_4^{2-} (mg L^{-1}; F) concentrations from 18th June 2012 to 6th September 2013 at Sutton and Strumpshaw Fen. Strumpshaw Fen was not visited in January 2013. Points represent mean values and error bars denote ± 1 standard error. * indicates where only Sutton Fen was sampled. # shows where samples at Sutton Fen were < LOD.

Table 15 Summary of porewater physicochemistry for all collars at Sutton and Strumpshaw Fen. All units are in mg L^{-1}, excluding NO_3^- (mg L^{-1} NO_3^--N), NH_4^+ (mg L^{-1} NH_4^+-N), SRP (mg L^{-1} SRP-P), pH and EC (µS cm^{-1}).

	Sutton Fen				Strumpshaw Fen			
	Mean	1 S.E.	Minima	Maxima	Mean	1 S.E.	Minima	Maxima
NO_3^-	0.05	0.01	0	0.53	0.12	0.03	0	1.2
NH_4^+	0.19	0.03	0	1.0	0.12	0.02	0	0.5
SRP	0.01	0.01	0	0.14	0.08	0.01	0	0.46
Cl^-	67	3.3	0	141	570	48	145	2103
SO_4^{2-}	2.8	0.67	0	44	14	2.1	0.22	81
DOC	39	3.5	0.1	167	23	1.9	0.1	89
DIC	65	5.0	0	216	68	5.0	0.1	146
pH	6.6	0.06	4.3	8.3	6.4	0.07	4.7	8.0
EC	784	26	385	1383	1912	1.1	652	4382
CO_2	201085	8888	15561	424353	180916	5726	34850	283858
CH_4	3490	436	46	23337	4139	493	72	22468
Fe^{2+}	0.83	0.09	0.07	6.5	0.29	0.05	0.04	2.3

Table 16 ANCOVA comparing porewater physicochemistry between sites with sampling months as a covariate. ** signifies a *p*-value <0.001, whilst * represents a *p*-value of <0.05.

	Independent variable (Site)		Covariate (Time)	
	F value	*p*-value	F value	*p*-value
NO_3^-	8.8748	<0.001**	1.1251	0.342
NH_4^+	10.4632	<0.001**	1.2318	0.263
SRP	37.237	<0.001**	1.001	0.454
Cl^-	138.0813	<0.001**	1.7749	0.052
SO_4^{2-}	31.2139	<0.001**	1.0709	0.389
DOC	28.6318	<0.001**	2.0291	0.022
DIC	2.6813	0.104	1.0412	0.416
pH	1.1469	0.147	0.7667	0.694
EC	107.8758	<0.001**	0.7063	0.755
CO_2	5.2505	0.023*	1.009	0.446
CH_4	0.5584	0.4561	0.8065	0.653
Fe^{2+}	19.2153	<0.001**	0.6417	0.815

When the models were run including the interaction terms between site and month, they were not significant.

Ditch water physicochemical parameters are shown in Figure 27 and 28. Ditch water dissolved CO_2 and CH_4, and EC showed a seasonal pattern, with the greatest concentrations observed during the summer months (Figure 27C; Table 17). EC was significantly greater at Strumpshaw Fen than at Sutton Fen (Table 18), by an order of magnitude (~ 500 μS cm^{-1} at Sutton and 500 – 2500 μS cm^{-1} at Strumpshaw over the 16 month period; Figure 27F). Sutton Fen had a significantly greater ditch pH than Strumpshaw Fen (Table 17 and 18) and both sites ditch pH's ranged between 7 and 8 (Figure 27C). DOC and DIC concentrations did not vary seasonally, although DIC concentrations were generally greater at both sites (Figure 27D; Table 17). DOC concentrations were significantly greater at Sutton Fen than at Strumpshaw Fen (Table 17 and 18), whilst DIC concentrations were significantly greater at Strumpshaw Fen than at Sutton Fen (Table 17 and 18). Ditch water NO_3^- concentrations peaked during winter months (Figure 28A), with mean concentrations of 0.5 and 0.7 mg L^{-1} NO_3^--N for Sutton and Strumpshaw, respectively. NO_3^- concentrations were significantly greater at Strumpshaw Fen than at Sutton Fen (Table 17 and 18). No seasonal trend was observed in NH_4^+, SRP, Cl^- and SO_4^{2-} concentrations, although concentrations were significantly greater at Strumpshaw Fen for all analytes apart from NH_4^+, which was significantly greater at Sutton Fen (Table 17 and 18).

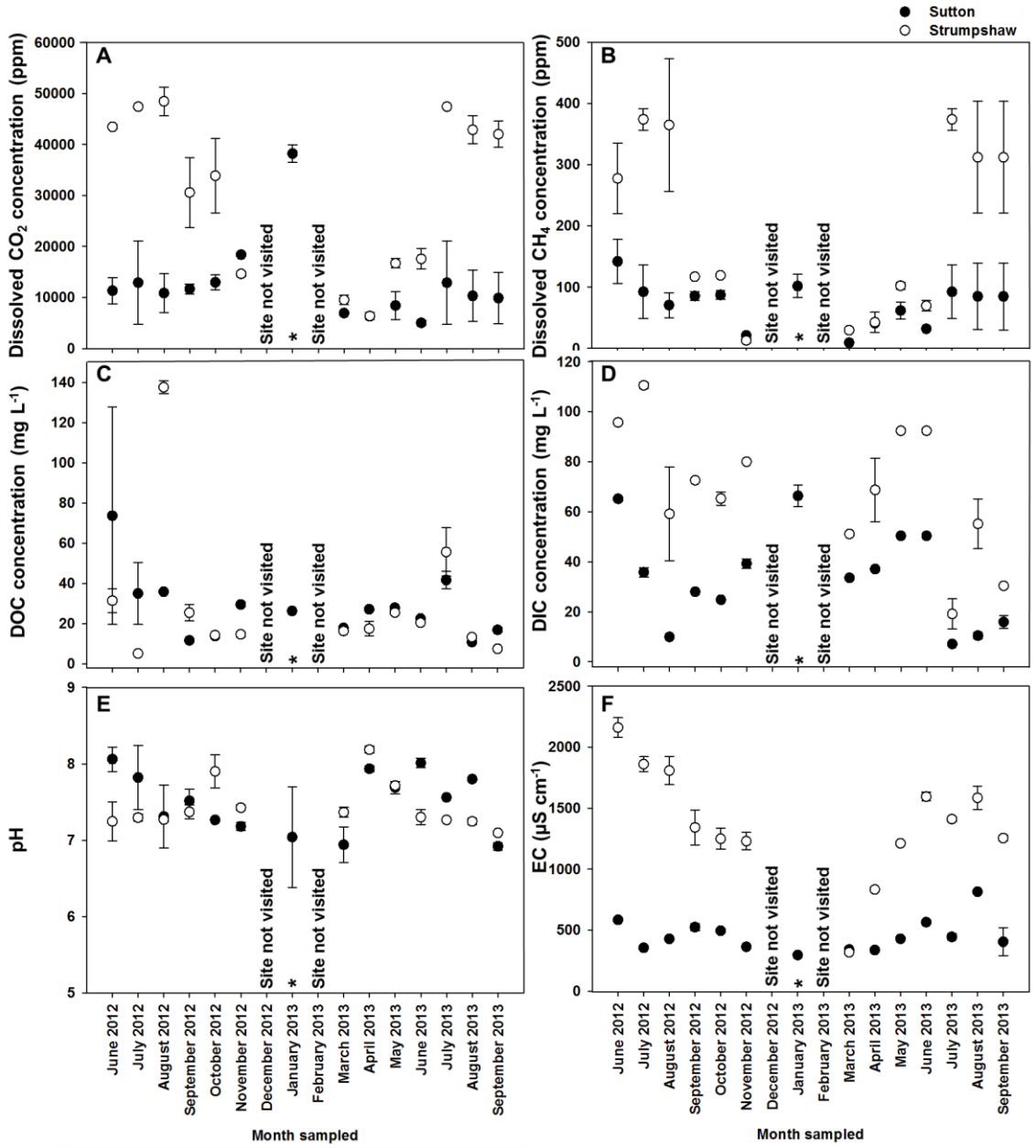


Figure 27 Monthly ditch water dissolved CO_2 (ppm; A), dissolved CH_4 (ppm; B), DOC (mg L^{-1}; C), DIC (mg L^{-1}; D), pH (E) and electrical conductivity (µS cm^{-1}; F) from June 2012 to September 2013 at Sutton and Strumpshaw Fen. Strumpshaw Fen was not visited in January 2013. Points represent mean values and error bars denote ± 1 standard error. * indicates where only ditches at Sutton Fen were sampled.

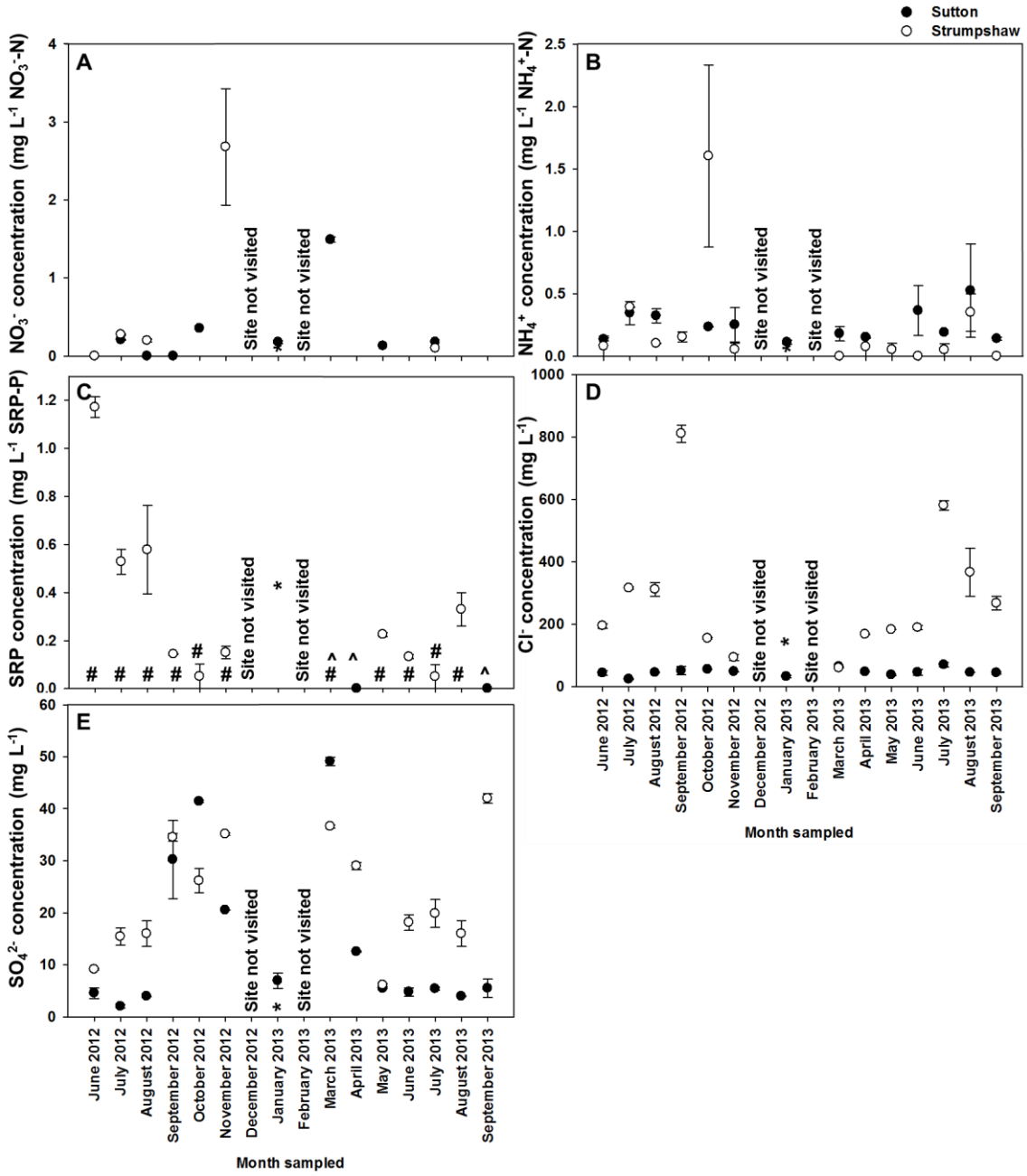


Figure 28 Monthly ditch water NO_3^- (mg L^{-1} NO_3^--N; A), NH_4^+ (mg L^{-1} NH_4^+-N; B), SRP (mg L^{-1} SRP-P; C), Cl^- (mg L^{-1}; D) and SO_4^{2-} (mg L^{-1}; E) concentrations from June 2012 to September 2013 at Sutton and Strumpshaw Fen. Strumpshaw Fen was not visited in January 2013. Points represent mean values and error bars denote ± 1 standard error. * indicates where only ditches at Sutton Fen were sampled. # and ^ show samples < LOD at Sutton and Strumpshaw Fen, respectively.

Table 17 Summary of ditch water physicochemistry for all collars at Sutton and Strumpshaw Fen. All units are in mg L^{-1}, excluding NO_3^- (mg $L^{-}NO_3^-$-N), NH_4^+ (mg $L^{-}NH_4^+$-N), SRP (mg L^{-}SRP-P), pH and EC (µS cm^{-1}).

	Sutton Fen				Strumpshaw Fen			
	Mean	1 S.E.	Minima	Maxima	Mean	1 S.E.	Minima	Maxima
NO_3^-	1.3	0.24	0	4.5	3.1	0.39	0.64	7.6
NH_4^+	0.23	0.08	0	2.2	0.88	0.32	0	5.6
SRP	0.01	0.01	0	0.17	0.10	0.05	0	1.4
Cl^-	63	4.2	27	128	40	5.4	3.8	120
SO_4^{2-}	138	30	2.0	595	39	3.2	14	72
DOC	17	2.8	1.5	62	12	1.7	0.74	35
DIC	39	4.0	5.7	83	50	4.2	6.8	76
pH	7.5	0.06	6.9	8	7.8	0.06	7.0	8.3
EC	844	115	378	3370	698	26	362	950

Table 18 ANCOVA comparing ditch water physicochemistry between sites with sampling months as a covariate. ** signifies a *p*-value <0.001, whilst * represents a *p*-value of <0.05.

	Independent variable (Site)		Covariate (Time)	
	F value	*p*-value	F value	*p*-value
NO_3^-	19.0568	<0.001**	0.5028	0.909
NH_4^+	6.9597	<0.001**	0.3895	0.965
SRP	12.6608	<0.001**	0.1603	0.999
Cl^-	17.3516	<0.001**	0.7075	0.744
SO_4^{2-}	15.138	<0.001**	0.636	0.809
DOC	4.2624	0.045*	0.2677	0.993
DIC	19.7739	<0.001**	1.3989	0.204
pH	17.1913	<0.001**	0.6471	0.799
EC	13.696	<0.001**	0.3147	0.986
When the models were run including the interaction terms between site and month, they were not significant.				

River water chemistry parameters are shown in Figure 29 and 30. The rivers at Sutton and Strumpshaw were relatively neutral, ranging between 7 and 8, and followed a seasonal pattern (Figure 29C). The River Yare and the Lackford run at Strumpshaw had a significantly higher pH during the 16 month sampling period (Table 19). Electrical conductivity (EC; Figure 29D), DOC (Figure 29A) and DIC (Figure 29B) also follow a seasonal pattern, with greatest concentrations observed during the summer months (Table 20). DOC and EC were significantly greater at Sutton than at Strumpshaw Fen over the sampling period (Table 19), whilst conversely DIC concentrations were significantly greater Strumpshaw Fen (Table 20). River NO_3^- concentrations peaked during the winter months (Figure 26A). The River Yare and the Lackford run (Strumpshaw Fen) had significantly greater NO_3^- concentrations (Table 19 and 20). NH_4^+, SRP, Cl^- and SO_4^{2-} concentrations in the rivers around Sutton and Strumpshaw Fen did not follow a seasonal pattern (Figure 30). The highest Cl^- concentration was observed in March 2013 in the River Yare and the Lackford Run. This coincided with the flood event in March 2013 (Figure 31 and 32) and a high tide. NH_4^+, Cl^- and SO_4^{2-} concentrations were significantly greater in the rivers around Sutton than around Strumpshaw Fen (Table 19 and 20), whilst SRP concentrations were significantly greater in the River Yare and Lackford Run (Strumpshaw Fen; Table 19 and 20).

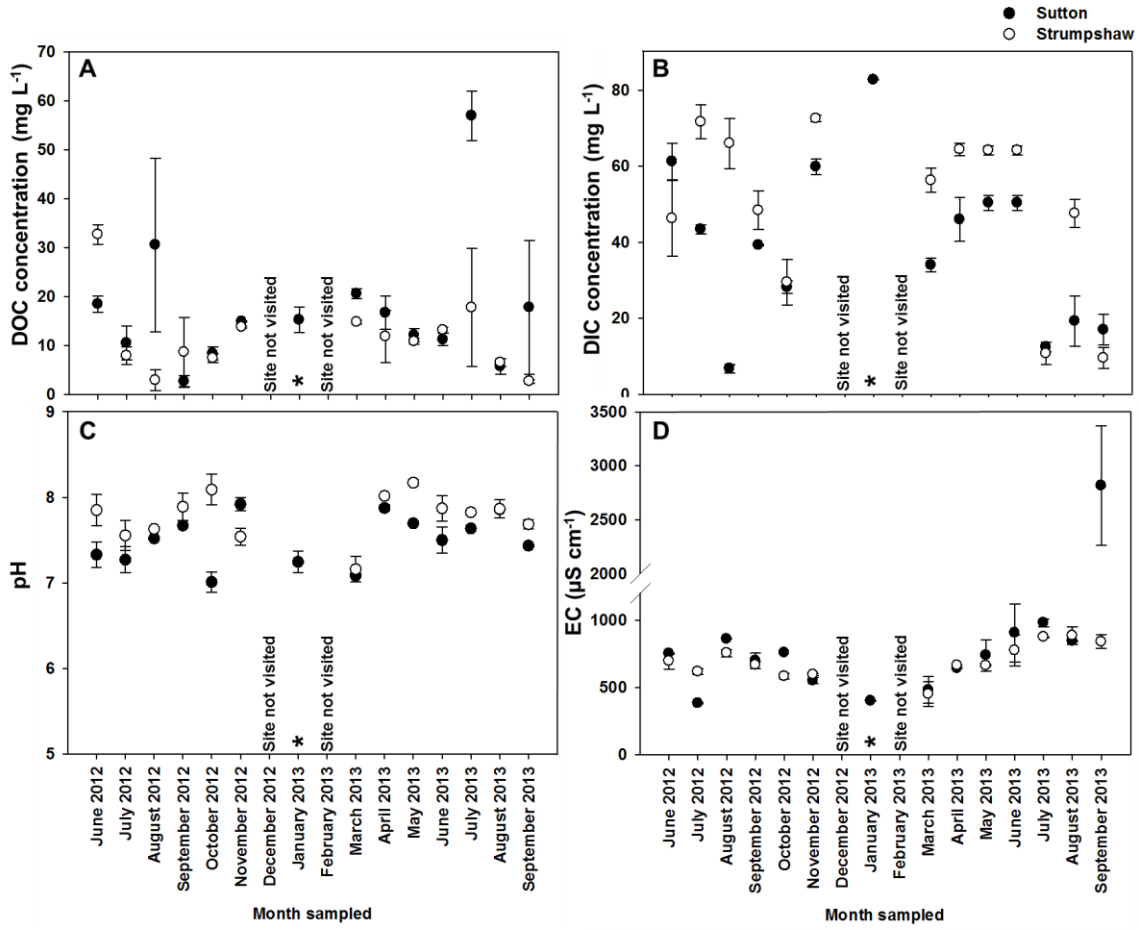


Figure 29 Monthly river water DOC (A), DIC (B), pH (C) and electrical conductivity (EC; D) from June 2012 to September 2013 at Sutton and Strumpshaw Fen. Strumpshaw Fen was not visited in January 2013. Points represent mean values and error bars denote ± 1 standard error. * indicates when only the River Ant and Sutton Broad were sampled.

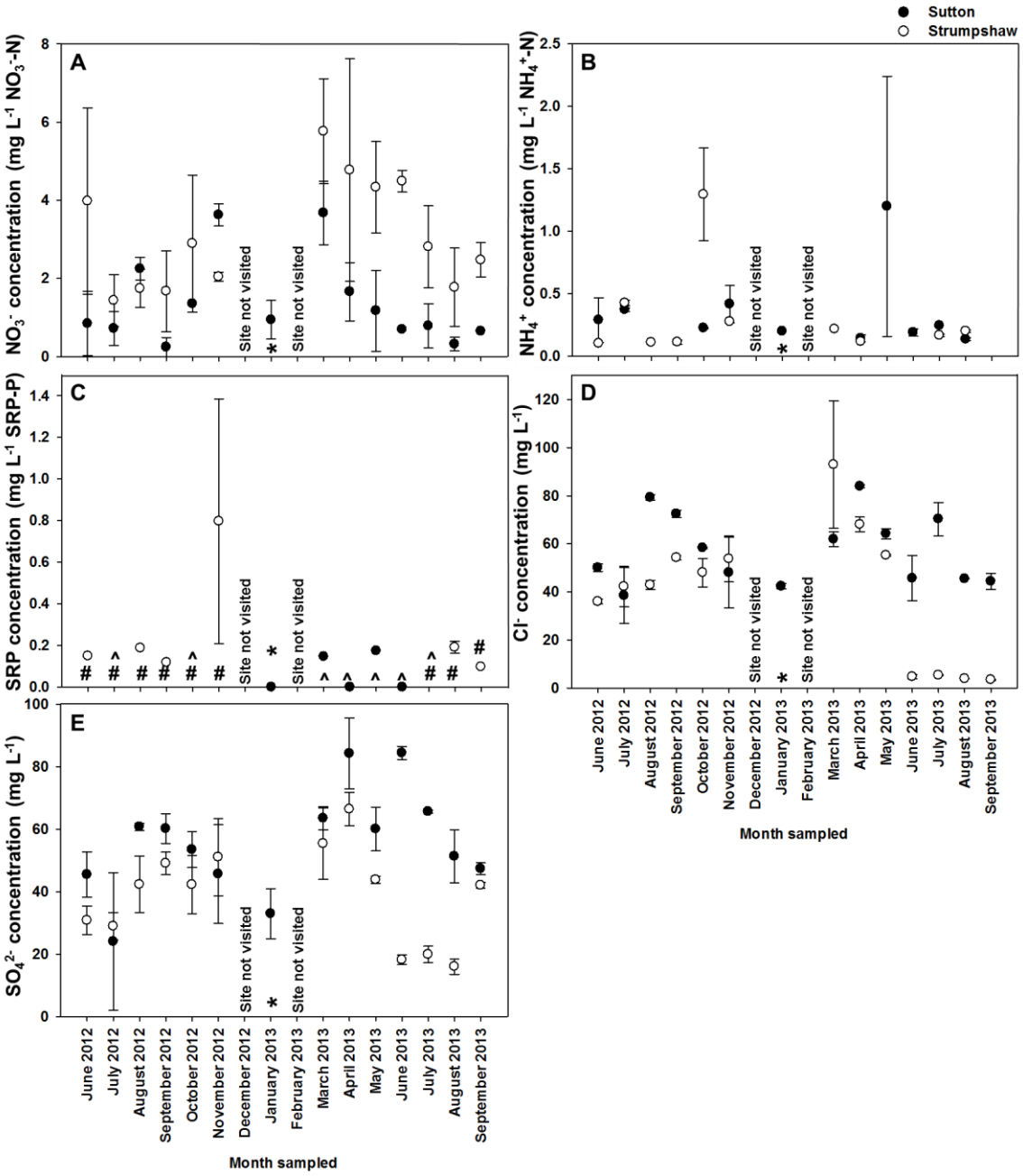


Figure 30 Monthly river water NO_3^- (A), NH_4^+ (B), SRP (C), Cl^- (D) and SO_4^{2-} (E) concentrations from June 2012 to September 2013 at Sutton and Strumpshaw Fen. Strumpshaw Fen was not visited in January 2013. Points represent mean values and error bars denote ± 1 standard error. * indicates where only the River Ant and Sutton Broad were sampled. # and ^ show samples < LOD at Sutton and Strumpshaw Fen, respectively.

Table 19 Summary of ditch water physicochemistry for all collars at Sutton and Strumpshaw Fen. All units are in mg L^{-1}, excluding NO_3^- (mg $L^{-}NO_3^-$-N), NH_4^+ (mg $L^{-}NH_4^+$-N), SRP (mg L^{-}SRP-P), pH and EC (µS cm^{-1}).

	Sutton Fen				Strumpshaw Fen			
	Mean	1 S.E.	Minima	Maxima	Mean	1 S.E.	Minima	Maxima
NO_3^-	1.3	0.24	0	4.5	3.1	0.39	0.64	7.6
NH_4^+	0.23	0.08	0	2.2	0.88	0.32	0	5.6
SRP	0.09	0.05	0	1.4	1.3	0.26	0	4.5
Cl^-	62	4.2	27	128	40	5.4	3.8	120
SO_4^{2-}	138	30	2.0	595	39	3.2	14	72
DOC	17	2.8	1.5	62	11	1.7	0.74	35
DIC	39	4.0	5.7	83	50	4.2	6.8	76
pH	7.5	0.06	6.9	8.0	7.8	0.06	7.0	8.3
EC	844	115	378	3370	698	26	362	950

Table 20 ANCOVA comparing river water physicochemistry between sites with sampling months as a covariate. ** signifies a *p*-value <0.001, whilst * represents a *p*-value of <0.05.

	Independent variable (Site)		Covariate (Time)	
	F value	*p*-value	F value	*p*-value
NO_3^-	19.0568	<0.001**	0.5028	0.909
NH_4^+	6.9597	0.011*	0.3895	0.965
SRP	29.9528	<0.001**	0.8517	0.606
Cl^-	17.3516	<0.001**	0.7075	0.744
SO_4^{2-}	15.138	<0.001**	0.636	0.809
DOC	4.2624	0.046*	0.2677	0.993
DIC	19.7739	<0.001**	1.3989	0.204
pH	17.1913	<0.001**	0.6471	0.799
EC	3.969	0.042*	0.3147	0.986
When the models were run including the interaction terms between site and month, they were not significant.				

3.3.7 Meteorological and environmental conditions

Meteorological conditions (Rainfall, incoming and outgoing solar radiation, PAR, air and peat temperature, relative humidity, wind speed and wind direction; Table 21) and water levels in the two fens were monitored between 18th June 2012 and 6th September 2013. Total daily rainfall (mm) and average daily temperature (ºC) are shown in Figure 23, whilst the remaining meteorological parameters are summarised within Table 21. Annual precipitation shown within Table 21 are for the entire year long period, unlike Figure 31, which shows only the 16 month sampling period. Distinct seasonal patterns are observed in average daily temperatures. Temperatures during the sampling period (June 2012 to September 2013) were on average lower than the 30 preceding years, except August 2012 (Met Office, 2013). Rainfall at the two sites was on average higher in 2012, yet lower in 2013 than the 30 years preceding (Met Office, 2013). A number of significant rainfall events occurred throughout the year, with 3 events exceeding a daily total of 20 mm. There was one day of especially heavy rainfall at both sites (10th March 2013) where 52.7 and 36.5 mm d^{-1} fell at Sutton and Strumpshaw, respectively.

Table 21 Meteorological parameters for Sutton and Strumpshaw Fen in 2012 and 2013.

	Sutton		Strumpshaw	
	2012	2013	2012	2013
Annual mean temperature (°C)	11	10	11	10
Annual precipitation (mm)	701	352	688	516
Annual mean soil temperature at 5 cm (°C)	11	10	11	10
Annual mean windspeed (m s^{-1})	1.9	2.1	1.5	1.5
Mean net radiation (W m^{-1})	56	69	59	57
Mean solar irradiation (W m^{-1})	144	143	117	110

Fen water levels also showed a clear seasonal pattern (Figure 24), with water levels drawn down below the peat surface in the summer due to plant uptake and greater evapotranspiration and water levels increasing above the peat surface during the autumn and winter months due to precipitation and fluvial inundation. The warmer weather and lower rainfall in summer 2013 caused a significant decrease in water level at both sites compared to summer 2012. Heavy rainfall events during the autumn and winter months, especially in January and March 2013, caused significant flooding of the sites during the winter. The rainfall event on 10th March 2013 caused the rivers Ant and Yare to overtop the bund at Sutton and Strumpshaw and flood the sites with large amounts of river water. This event also left a significant amount of water on Strumpshaw Fen until May 2013.

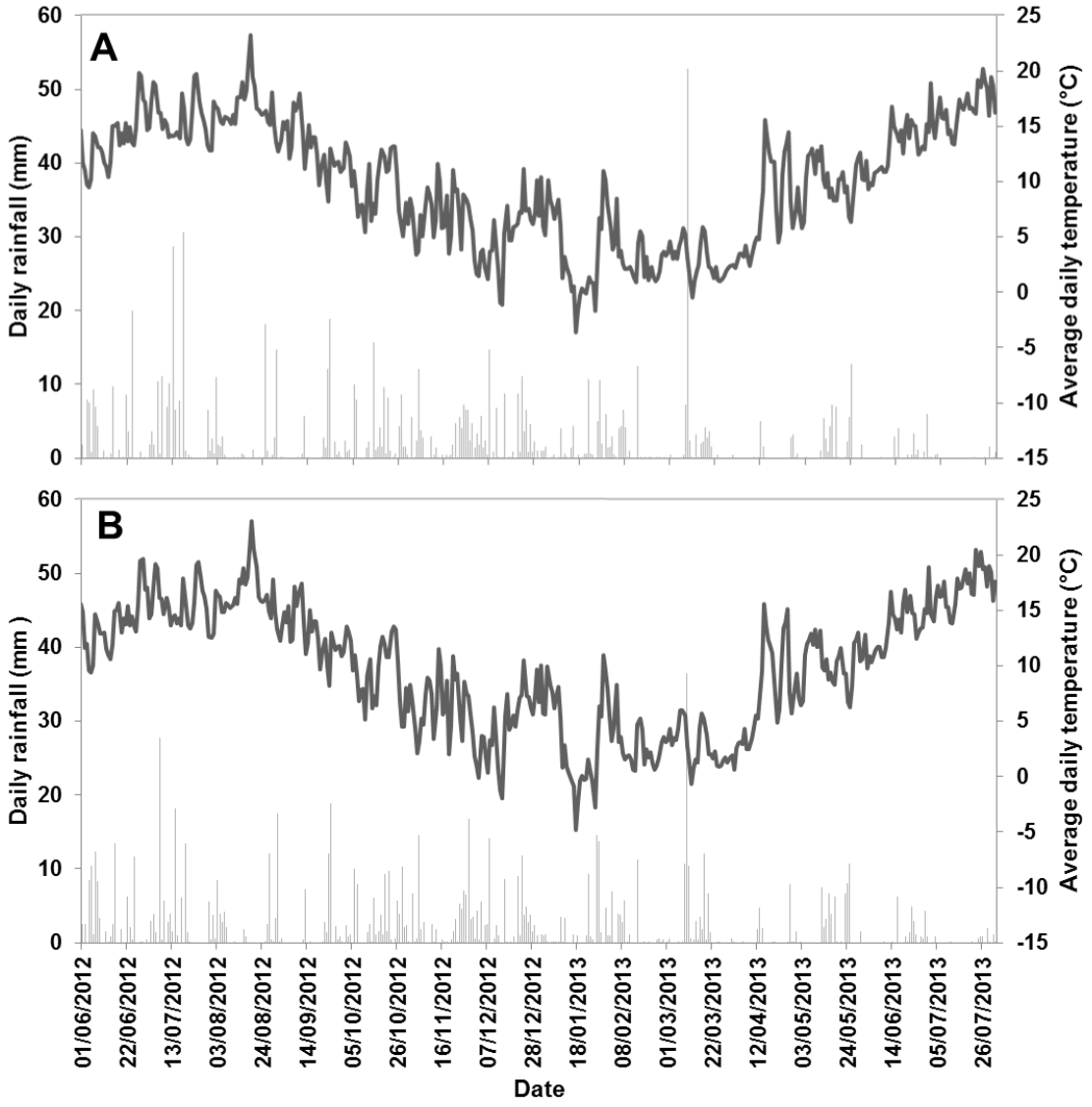


Figure 31 Sutton (A) and Strumpshaw (B) Fen total daily rainfall (mm) and average daily air temperature (°C) data from June 2012 to September 2013.

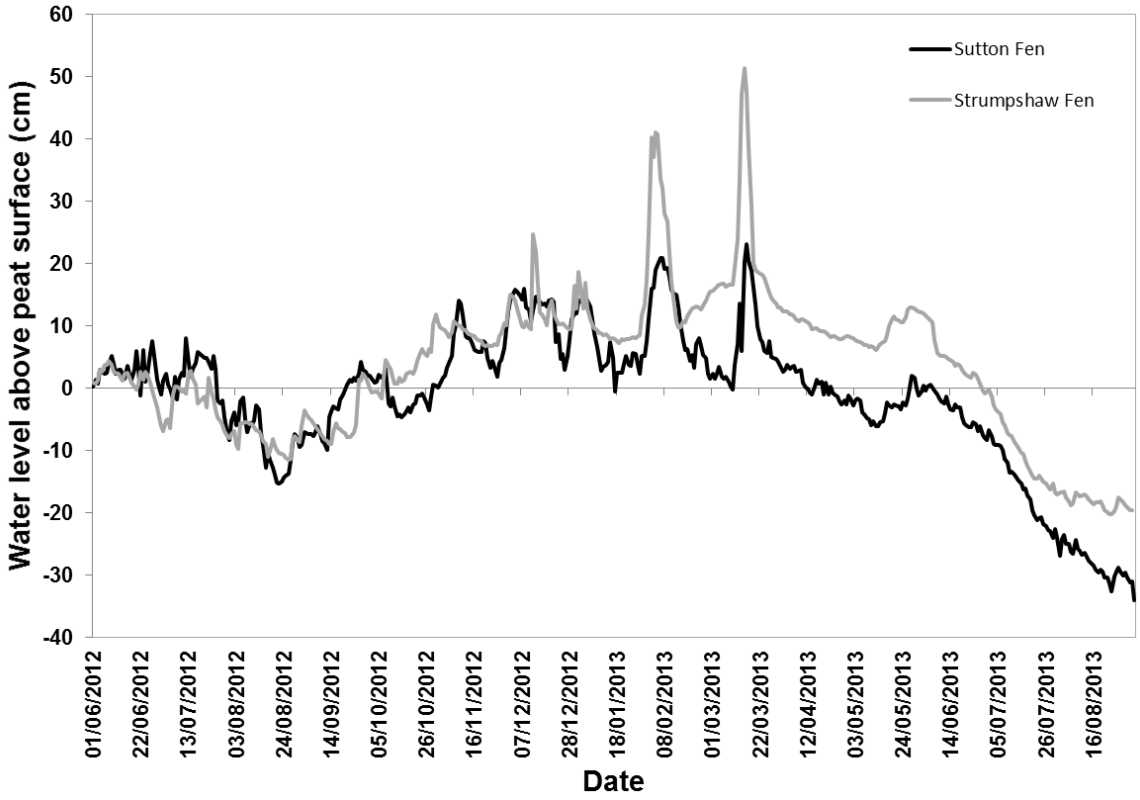


Figure 32 Sutton and Strumpshaw Fen water levels from June 2012 to September 2013.

3.4 Discussion

This chapter described the two floodplain fen sites chosen to sample GHG exchange and sought to establish the difference in nutrient status between the two selected sites, using the following research question and hypothesis:

R.Q.1. What is the nutrient status of Sutton and Strumpshaw fens?

H_1: Strumpshaw Fen will have greater peat N and P contents than Sutton Fen.

H_2: Strumpshaw Fen will have greater foliar N and P contents than Sutton Fen.

H_3: Strumpshaw Fen will have greater porewater NO_3^- and SRP concentrations than Sutton Fen.

To establish if there was a difference in nutrient status, foliar and peat N and P contents and porewater nutrient concentrations were investigated.

3.4.1 Differences in peat nutrient contents

Peat nutrient contents quantified from triplicate 3 m cores taken in June 2013 showed a significant difference in K contents only between sites (Table 10). However, a significant difference in surface (< 0.15 m below peat surface) peat N and P contents was observed in samples taken in both March 2013 and June 2013. Therefore, H_1 was partially rejected. Non-significant differences in N and P contents in peat cores from Sutton and Strumpshaw fen may be caused due to similar contents being found below depths of 0.2 m. As peat accumulates slowly, generally between 0.5 and 1 mm $year^{-1}$ (Keddy, 2010), contents from below a depth of 0.2 m are likely to be from before 200 years BP, prior to intensification of agriculture via fertiliser application and anthropic pollution. Therefore, N and P contents are similar throughout the majority of the 3 m profile and not found to be statistically different. However; surface peats (< 0.15 m below the peat surface) did exhibit significant differences between sites. It is this surface portion which undergoes water table draw down during the summer months (Figure 32), allowing this portion if the peat profile to become oxic and potentially increase heterotrophic respiration and aerobic CH_4 oxidation. In March 2013, both N and P contents were significantly greater at Strumpshaw Fen than at Sutton Fen (Table 11), as anticipated due to modern anthropic influence. P contents are still significantly greater at Strumpshaw Fen than at Sutton Fen (Table 11); however, N contents are no longer significantly greater at Strumpshaw Fen. It is hypothesised that the flood event that occurred in March 2013 (Figure 32) inundated Sutton Fen with mineral content in the form of sediment washed off the local farm land and thus altered the surface peat N contents. This sudden increase in N was not observed in the river water in March 2013 (Figure 30) as it may have been deposited onto the fen in a sediment-bound form and not bioavailable. When water samples were filtered, the mineral content was removed.

An increase in bulk density and a decrease in LOI at Strumpshaw Fen between 0.2 to 0.3 m below the surface indicate a possible flood event or migration of the river within the floodplain depositing more mineral material on the fen (Lambert et al., 1960). This also coincides with a decrease in C:N ratios and an increase in N:P ratios. A similar alteration to the LOI was also observed at Sutton Fen at a depth of 0.3 m, although there was not a pronounced increase in bulk density and N:P ratios during the same period (Figure 16). It is thought that a flood event occurred at this depth; however, due to the lesser historical management and human interference with Sutton Fen, the bulk density was not altered as the site had not undergone compaction. Additionally, the increase in C:N ratio at 0.3 m depth indicates that the fluvial deposits on the fen were more C rich than at Strumpshaw Fen.

3.4.2 Differences in foliar nutrient contents

Foliar N and P contents were significantly greater at Strumpshaw Fen than at Sutton Fen (Table 14) and therefore, H_2 was accepted. The difference in contents reflects the significantly different nutrients concentrations found within river, ditch and porewater (Table 16, 18 and 20) between sites. With greater nutrient concentrations/contents within the porewater and surface peat, plants can take up more bioavailable N and P for primary and secondary metabolism, resulting in greater foliar N and P contents. The differences in water level management between the two sites is a contributing factor to the differences in foliar N and P contents, as the opening of the sluice gates at Strumpshaw Fen during December will allow the movement of nutrient enriched water onto the fen. Despite river water concentrations not being analysed in December 2012, river water concentrations in November 2012 were greater than the preceding months (Figure 30).

Vegetation at Strumpshaw Fen was generally N limited (Figure 23). The N limitation in vegetation at Strumpshaw Fen is caused by the high P inputs of anthropic origin from the river over the past century. Fertiliser application, pastoral farming, industrial inputs and lack of P removal from sewage have resulted in the site being loaded with P, shown in the surface peat (Figure 17C). Sutton Fen showed half of the collars analysed to be N limited, whilst the remaining 3 collars were P limited (Figure 23). These differences in foliar N and P limitation at Sutton Fen may be due to differences in vegetation composition, as different plant species store different nutrient contents within their leaves. However, it may also be due to the significantly lesser N and P contents at the site (Table 14) making the ratios more variable than at Strumpshaw Fen. The difference in N and P limitation between collars also shows the greater species diversity at Sutton Fen, as greater species diversity is often a sign of nutrient poorer conditions (Wassen and Olde Venterink, 2006, Koelbener et al., 2010). Additionally, there was a lesser dominance of taller reeds at Sutton Fen than at Strumpshaw Fen, thus reducing the competition by shading on other vascular plants and allowing greater competition between lower lying vegetation. The difference in vegetation was not only seen in the species diversity, but also the significant difference in plant height and aboveground green biomass between sites (Section 3.2.4). Greater porewater nutrient availability at Strumpshaw Fen than at Sutton Fen will have facilitated growth and aboveground biomass production at the site, as nutrient enrichment increases productivity within peatlands (Koelbener et al., 2010).

3.4.3 Differences in porewater chemistry

Porewater nutrient concentrations were quantified over the 16 month sampling period for both Sutton and Strumpshaw Fen. Porewater NO_3^- and SRP concentrations were found to be significantly greater at Strumpshaw Fen than at Sutton Fen (Table 16) and resulted in H_3 being accepted. Additionally, this significant difference in NO_3^- and SRP was also observed in ditch and river water for the two sites, with the rivers and ditches that feed Strumpshaw Fen having significantly greater concentrations (Table 18 and 20).

The difference in management between the two sites, especially regarding the management of water levels at the two sites, will have a large impact on the porewater quality. There is a history of nutrient inputs via fluvial inundation at Strumpshaw Fen. The larger catchment of the River Yare may be a causal factor in the greater N and P concentrations in pore-, ditch and river waters. The rivers that flow adjacent to the sites provide nutrients to the site, via over bank flooding and from the opening of the sluice gates in December, for plants to utilise for growth and for microbial processes. N and P have been shown to alter mineralisation processes, such as heterotrophic respiration, methanogenesis and methanotrophy (Amador and Jones, 1993, Aerts and Toet, 1997, Aerts and de Caluwe, 1999, Min et al., 2011). The significantly lower porewater DOC concentrations and the significantly higher porewater dissolved CO_2 concentrations at Strumpshaw fen may suggest greater rates of heterotrophic respiration, fermentation and methanotrophy at the site. However, more research on the relationship between NO_3^- and SRP on respiration, fermentation and methanotrophy is needed to fully understand the relationship, especially as the quality of the DOC was not investigated in this study. DOC quality has been shown in other studies to have a larger control on heterotrophic respiration than NO_3^- and SRP inputs (Chasar et al., 2000).

The greater porewater dissolved CO_2 concentrations at Strumpshaw Fen than at Sutton Fen may be linked to NO_3^- and SRP concentrations; however, there were also significant differences in Cl^-, SO_4^{2-} and Fe^{2+} between the sites. It would be expected, that dissolved CO_2 concentrations would be lower at Strumpshaw Fen due to the greater SO_4^{2-} and Cl^- concentrations than at Sutton Fen, as salinity reduces CO_2 solubility within water (Weiss, 1974). This indicates that there must be significantly greater production rates of CO_2 to supersaturate the porewater more at Strumpshaw Fen than at Sutton Fen. Fe^{2+} was used as a proxy for the porewater redox conditions, with higher concentrations showing more reduced conditions. Sutton Fen had significantly greater Fe^{2+} concentrations than Strumpshaw Fen, indicating more reduced conditions at the site. The significantly greater

concentrations for NO_3^- at Strumpshaw Fen will have increased the redox potential at the site. The more reduced conditions at Sutton Fen than at Strumpshaw Fen may have resulted in lesser dissolved CO_2 concentrations.

Dissolved porewater CH_4 concentrations were not significantly different between sites, possibly indicating the occurrence of anaerobic CH_4 oxidation (AOM), the inhibition of methanogenesis by NO_3^- or the transport of CH_4 from an aqueous solution to a free-phase gaseous form. SO_4^{2-} and NO_3^- have been shown to be used as terminal electron acceptors in anaerobic CH_4 oxidation in peatlands sites (Smemo and Yavitt, 2011, Blazewicz et al., 2012, Gupta et al., 2013). Significantly greater SO_4^{2-} and NO_3^- concentrations at Strumpshaw Fen than at Sutton Fen may result in greater rates of AOM and the production of more CO_2. SO_4^{2-} and NO_3^- have also been shown to be methanogenic inhibitors as the two macronutrients are toxic to methanogenic archaea (Roy and Conrad, 1999, Smemo and Yavitt, 2011). CH_4 is sparsely soluble in water; however, salinity reduces CH_4 solubility (Yamamoto et al., 1976). However, an isotopic study would be necessary to confirm the occurrence of AOM at Sutton and Strumpshaw Fen.

3.4.4 Differences in vegetation at Sutton and Strumpshaw Fen

Differences in peat, foliar and porewater nutrient contents/concentrations, as well as water levels (Figure 32) result in differences in vegetation between the two sites. Strumpshaw Fen has a larger abundance of *P. australis* and a lower species diversity (Table 12). Higher nutrient status is often a causal factor for the dominance of *P. australis* and poorer species diversity (Wassen and Olde Venterink, 2006, Koelbener et al., 2010). This is mirrored in the aboveground green biomass and average plant height, which were significantly greater at Strumpshaw Fen (Section 3.3.4). This greater green area may result in greater rates of CO_2 sequestration at the site, especially with the greater N foliar contents, as greater N contents have been shown to increase sequestration rates (Liu and Greaver, 2009). The higher species diversity at Sutton Fen is represented in Figure 19 by the larger spread in the y axis. This greater species diversity corroborates with the poorer peat, foliar and porewater N and P contents/concentrations at Sutton Fen (section 3.3.2 to 3.3.6). Additionally, *P. coloratus* in collar 6 at Sutton Fen does not have an effect on plant species observed between sites (Figure 19). The occurrence of *P. coloratus* only effects the y axis spread and not the x axis spread, where the difference between the two sites is seen (Figure 19). *P. coloratus* is usually a sign of mire conditions; however, this is not the case at collar 6 at Sutton Fen, where the collar was located in a

slight depression and was therefore waterlogged for a longer period of time than other collars. These differences in vegetation between the two sites may affect CO_2 sequestration rates and subsequently whether the sites are net C sources or sinks.

3.5 Summary and synthesis

Analysis of peat, foliar and pore-, ditch and river water nutrient status showed significant differences between sites (R.Q.1). These differences in surface peat, foliar and porewater nutrient contents/concentrations show Strumpshaw Fen to be more nutrient enriched than Sutton Fen (R.Q.1). Surface peat (< 0.15 m below peat surface) at Strumpshaw Fen was found to have significantly greater N and P contents than at Sutton Fen. However, this difference was not observed within the 3 m cores taken in June 2013, leading to H_1 being partially rejected. Foliar N and P contents were significantly greater at Strumpshaw Fen, resulting in H_2 being accepted. The difference in foliar N and P contents did not lead to a strict difference in nutrient limitation between sites. Vegetation at Strumpshaw Fen was generally N limited, whilst collars at Sutton Fen were half N limited and half P limited. The anthropic inputs of P into the rivers around Strumpshaw have loaded the site with P. These differences in foliar N and P contents and nutrient limitations may have an effect on photosynthetic rates for the sites. Finally, a significant difference in porewater NO_3^- and SRP concentrations were observed and H_3 was accepted. In addition to H_3, ditch and river water NO_3^- and SRP concentrations were also significantly greater at Strumpshaw Fen.

4. Greenhouse gas exchange and controlling factors on carbon fluxes in floodplain fen sites of contrasting nutrient status.

4.1 Introduction

This chapter presents observed greenhouse gas (GHG) exchange data (CO_2 exchange and CH_4 emission via diffusion, plant-mediated transport and evasion) and controlling factors analysis on C exchange. The following research questions (R.Q.) and hypotheses (H) will be answered in this chapter:

R.Q.2. How do CO_2 and CH_4 fluxes from Sutton and Strumpshaw Fen compare to European floodplain fens?

R.Q.3. What are the controlling factors on CO_2 and CH_4 emissions from floodplain fens?

H_4: R_{eco} will be controlled by peat temperature, VGA, water level and porewater NO_3^- and PO_4^{3-} concentration.

H_5: GPP will be controlled by air temperature, PAR, VGA, water level and porewater NO_3^- and PO_4^{3-} concentration.

H_6: CH_4 emission will be controlled by peat temperature, VGA, water level, redox conditions, barometric pressure, and porewater NO_3^- and PO_4^{3-} concentration.

GHG exchange was measured between 18th June 2012 and 6th September 2013 *in situ* using static chambers (sections 4.2.1 and 4.2.5) and an infrared gas analyser (IRGA). Firstly, the methods used to quantify GHG exchange and controlling factors on C exchange are presented in section 4.2. Subsequently, section 4.3 reports a general description of observed carbon (C) exchange at two floodplain fen sites of differing nutrient status (chapter 3) and outlines controlling factors on C exchange. Sections 4.3.1, 4.3.2 and 4.3.3 report fen CO_2 exchange, environmental variables associated with CO_2 exchange and ditch CO_2 evasion, respectively. Sections 4.3.4 and 4.3.5 present fen CH_4 emissions (diffusive and plant-mediated fluxes) and ditch CH_4 evasion, respectively. Section 4.3.6 outlines the controlling factors on fen C exchange. Section 4.4 discusses fluxes and controlling factors. Finally, section 4.5 summarises and synthesises the results.

4.2 Methodology

GHG exchange was quantified between 18th June 2012 and 6th September 2013 (R.Q.2). Initially it was intended to measure N_2O fluxes throughout the sampling period; however, N_2O concentrations were below detectable levels in the chambers. Thus, CO_2 and CH_4 became the focus of the field studies.

There are two main methods to quantify GHG exchange; enclosure and micrometeorological techniques. Eddy covariance is a micrometeorological technique that uses anemometers and gas sensors attached to a flux tower to calculate a vertical gas flux over a large landscape scale (Denmead, 2008). This method uses high frequency measurements to calculate a flux under the assumption that all eddies transporting gas are accounted for (Baird et al., 2010). Disadvantages of this method include assumptions that fluxes are constant with height and concentrations change vertically and not horizontally, calibration or equipment failures, difficulties in measuring vertical wind speeds and gas concentrations simultaneously, flux footprint alterations with alterations in wind speed and direction, and difficulties in measuring fluxes over small spatial scales (Moffat et al., 2007b, Denmead, 2008, Baird et al., 2010).

Enclosure techniques, such as dynamic/open chambers and static/closed chambers, provide smaller scale, highly sensitive flux measurements more suitable to peatlands. A flux chamber is made up of two main components, a static collar that is inserted into the peat substrate and provides a frame for the removable chamber lid (Fig 10). The basic principle of flux-chambers is to restrict the volume of air in which gas exchange occurs to magnify changes in gas concentrations in the headspace (Denmead, 2008). This can be done using a dynamic/open method, whereby a constant flow of atmospheric air is maintained through the chamber headspace and the difference in gas concentration entering and leaving the headspace is measured using an online gas sensor, such as an IRGA (Denmead, 2008). The circulation of atmospheric gas through the system reduces perturbations to natural diffusion rates that can be caused in systems without circulation. This circulatory system also provides difficulties in flux calculations, as when gas exchange rates are small, it can be difficult for the online gas sensors to detect changes in concentrations. Furthermore, the systems are often automated and require a power supply to flush the headspace and for the online gas sensors, as well as expensive to deploy.

Static or closed flux chambers are a simpler and more cost-effective method that use alterations in headspace gas concentrations over a specific time period as a means for flux calculation. This requires samples to be taken from a port at specific time periods and analysed in a laboratory later on (Pumpanen et al., 2004, Denmead, 2008). Static systems do present a number of disadvantages due to the closed design – alterations to exchange rates can be caused by the creation of a microclimate within the chamber, altering air and substrate temperature; pressure differences between the inside and outside of the chamber and an increase in gas concentration in a chamber (Pumpanen et al., 2004, Denmead, 2008). Furthermore, the heterogeneity of the peat substrate and the small surface area of the chamber result in large coefficients of variation and require replicates to be able to calculate viable fluxes (Denmead, 2008). However, static chambers are used more often than dynamic systems as it is easier to detect concentration alterations, the systems are mechanically simpler, much more portable and inexpensive to build (Denmead, 2008). For these reasons, a closed flux chamber was used at both Sutton Fen and Strumpshaw Fen.

4.2.1 Tall static flux chamber design

Important design considerations need to be taken into account when it comes to designing a static flux chamber, including: vegetation height, construction materials, enclosure geometry, barometric air pressure, air and peat substrate temperature, gas tightness and ensuring the mixing of air within the chamber (Denmead, 2008). Methods for achieving a gas tight connection between a collar and chamber include: a water-filled gutter (Hendriks et al., 2007), foam gaskets and clamps (Whiting and Chanton, 2001), air tight overlaps and abutting joints (Matson and Harriss, 1995). For this research project a silicone foam seal was used as it provides a gas-tight seal whilst minimising disturbance to the peat during sampling. Furthermore, chambers and collars for this research project were made from plastics inert to CO_2 and CH_4. Collars were constructed from sheets of 3 mm thick polyvinylchloride that were bolted together in each corner and sealed with marine grade silicone sealant (Dow Coring). At each site, six collars (60 x 60 x 20 cm - width x height x depth; Figure 10B) were inserted to a depth of 18 cm in pairs approximately 10 m apart from each other in areas best representing the variation in vegetation in the delineated sections of cut reed chosen at both each site. The height of the collar above the peat surface was taken into account at each site as not to create an artificial environment where water could either be stored or prevented from flowing into the collar when deciding on the collar insertion depths.

Unlike previous studies of GHG exchange in reeds (Hendriks et al., 2007), the vegetation was not cut to fit the size of the chamber as this can create artificial GHG exchange rates. Instead a tall static flux chamber was designed to accommodate the height of the reeds at both sites. A segmented chamber (Figure 10A) was designed for ease of deployment in the field, with a total height of 1.5 m and each segment 40 cm in height and the top segment 30 cm. The chamber has a basal area and volume of 0.36 m^2 and 0.54 m^3 respectively. Gas tight seals between each segment and the lid were achieved using silicone foam that each segment rests upon (Figure 10C). The weight of the chamber alone was sufficient to provide a gas tight seal. The gas tightness of the chamber was tested in the laboratory using steam and smoke in February 2012. Five holes were drilled into the chamber lid for: a meter to measure temperature, humidity and barometric pressure (Commeter C4141, stated manufacturer's accuracy of ± 0.4 °C and ± 0.01 kPa) fitted to a 31 mm base-diameter rubber bung, a pressure equalisation balloon, an inlet and an outlet for an IRGA (PP Systems, MA, USA, CIRAS-2) using three-way stopcocks (Cole Palmer) and a 1.5 m length of tygon tubing (3.2 mm inner diameter (i.d.)) to allow for headspace sampling. A shroud was made of black polypropylene plastic to cover the chamber to allow for soil respiration (R_{eco}) rates to be quantified. Four fans were attached to each chamber and operated during sampling to promote the full mixing of gas within the closed headspace. Ice packs were also used during the warmer months to try to minimise the impact of solar warming on the enclosed headspace and reduce the potential disturbance on rates of GHG exchange. Duckboards were laid at each collar to reduce observer induced alterations to GHG exchange rates.

4.2.2 GHG exchange measurements using tall static chambers

Flux measurements using tall static chambers were taken between 18th June 2012 and 6th September 2013. Samples were collected over a five day period every month between 09:00 and 17:00 (GMT) in order to answer R.Q.2. During sampling, the observer remained on the duckboards to reduce artificial GHG exchange rates. Before assembling the chamber, fans and ice packs were attached and switched on and the IRGA was attached to the chamber lid. Whilst assembling the chamber, the lid was held up in the air to flush the system, including the IRGA, with atmospheric air. Once the IRGA stabilised at atmospheric CO_2 levels and the lid was placed on the chamber. Measurements of ecosystem respiration (R_{eco}) required a shroud to be placed over the chamber. This was done just after the lid was placed on the chamber. The IRGA was started, the sample tube was then purged (45 mL deadspace removed), the syringe was then pumped fully three times to ensure a well-mixed air samples was taken and then the sample was taken. Each sample was transferred to a pre-evacuated exetainer

(Labco Limited) via a three way stopcock and a needle. A 15 ml headspace sample was then extracted every 2 minutes thereafter for 20 minutes, with the sample tube being purged every time.

For measurements of net ecosystem exchange (NEE) and CH_4, the same procedure was followed as for R_{eco} but no shroud was placed on the chamber. A further 4 15 ml headspace samples were taken every 10 minutes for 60 minutes after the initial 20 minutes to achieve a significant increase in CH_4 to calculate a flux from. All headspace samples were transferred into pre-evacuated exetainers, which were analysed off-site in the laboratory (section 4.2.3). Pressure, temperature and humidity readings were recorded after each sample extraction to compensate for pressure and temperature in the flux calculation (see section 4.2.6).

4.2.3 Laboratory analysis of CO_2 and CH_4

Headspace samples were analysed in the laboratory using a Gas Chromatograph coupled with Flame Ionization Detector and methanizer (GC-FID; Agilent Technologies 7890A GC system; zero grade N_2 carrier gas at 25 mL min^{-1}, zero grade H_2 (30 mL min^{-1}) and air (moisture and hydrocarbon-free; 400 mL min^{-1}) auxiliary gases, operated at 300°C; 1.8 m Propak Q chromatographic column with 80/100 mesh heated to 40°C). Gas standards and drift checks were made up from an air mix (Scientific and Technical Gases Ltd – 98.7 ppm CH_4 and 3706 ppm CO_2) and diluted down using oxygen-free Nitrogen (BOC), taking temperature and barometric pressure into account. 15 mL of gas was injected into pre-evacuated exetainers submerged in water to prevent atmospheric air from contaminating the standards, drift checks and blanks (Hamilton and Ostrom, 2007). For each run on the GC, a linear regression was fit through the standards to produce a calibration curve and was applied to samples in the run. Drift checks were used to monitor short-term drift in the GC (Table 22) and results were rejected if > ± 10 %.

Table 22 GC average RSDs (%) for short-term analytical drift for CO_2 (174 ppm) and CH_4 (0.8 ppm).

Detector	CO_2	CH_4
FID	6.4	5.5

4.2.4 Measuring Vascular Green Area

To help understand gross primary production (GPP), the vascular green area (VGA) of vegetation was measured. Different methods have been used in the literature to monitor phonological changes, including harvesting plant biomass (Moore et al., 2002) and measuring plant biomass *in situ* (Wilson et al., 2007a). Despite harvesting methods providing more accurate results of VGA, a non-destructive method is needed for GHG exchange research, where intact vegetation is needed to follow seasonal dynamics of photosynthesis and respiration within a known area (Laine et al., 2007a, Wilson et al., 2007a). Hence the Wilson et al. (2007a) method was selected. VGA was measured by counting the stems and leaves of each plant species within the collars at both sites, paying attention not to pull on any vegetation, throughout the study period. In the areas surrounding each collar, 3 samples of each species were selected and had their stem length and width measured. Three leaves were also selected and measured (width and length). The surface area of leaves was calculated using species-specific formulae (Table 23) based on the geometrical shape of each species.

Stem surface areas (if present) were calculated using Eq. 15.

$$S_{ga} = (2 \cdot \pi \cdot r) \cdot h \qquad \text{Eq. 15}$$

where S_{ga} is the stem surface area (m^2), r is the stem radius (m) and h is the stem height (m). The leaf and stem areas were then averaged per plant species. Species VGA was calculated (Eq. 16) by multiplying average leaf and stem surface areas by the number of leaves and stems in each collar and summing the values for all species to give the VGA in $m^2\ m^{-2}$ (Chivers et al., 2009):

$$VGA = (La \cdot Ln) + (Sa \cdot Sn) \qquad \text{Eq. 16}$$

where La is the average leaf area (m^2), Ln is the average number of leaves, Sa is the average stem area (m^2) and Sn is the average number of stems. Detailed field-based surveys were undertaken by Andrew Skinner from RSPB in July 2012 to confirm plant species identified (section 3.3.3).

Table 23 Species-specific leaf shape for leaf area calculation: Ellipse ($\pi \cdot r_1 \cdot r_2$), half cone ($r \cdot L \cdot \frac{\pi}{2}$), rectangle ($W \cdot L$), triangle ($0.5 \cdot W \cdot L$) and circle ($\pi \cdot r^2$), where *W* = width, *r* = radius and *L* = length of leaf. Formulae are taken from (Wilson et al., 2007a).

Plant species	Leaf shape
Berula erecta (Huds.) Coville (1893)	Ellipse
Calamagrostis canescens L. (Weber) Roth (1789)	Half cone
Calystegia sepium (L.) R. Br. (1810)	Half cone
Carex acutiformis Ehrh. (1789)	Half cone
Cladium mariscus (L.) Pohl (1809)	Half cone
Eupatorium cannabinum L. (1753)	Ellipse
Galium palustre L. (1753)	Rectangle
Hydrocotyle vulgaris L. (1753)	Circle
Juncus subnodulosus Schrank (1789)	N/A
Lysimachia vulgaris L. (1759)	Half cone
Mentha aquatica L. (1759)	Triangle
Myrica gale L. (1759)	Half cone
Peucedanum palustre (L.) Moench (1794)	N/A
Phalaris arundinacea L. (1759)	Half cone
Phragmites australis (Cav.) Trin. ex Steud (1841)	Half cone
Rumex hydrolapathum Huds. (1778)	Ellipse
Scutellaria galericulata L. (1753)	Triangle
Thelypteris palustris Schott (1834)	Triangle
Typha latifolia L. (1753)	Rectangle

4.2.5 Measuring C evasion using closed floating flux chambers

A number of methods to quantify GHG evasion rates have been used, including gas exchange coefficients (Hope et al., 2001, Hope et al., 2004) and floating flux chambers (Billett and Moore, 2008, Billett and Garnett, 2010, Dinsmore et al., 2010). Kremer et al. (2003) also suggested the use of eddy covariance as a method to quantify evasion rates, but this method has not yet been used. Gas exchange coefficients use the concentration gradient between the surface water and the air and the physical transfer or turbulent energy at this interface to calculate evasion rates. The equation for this method does provide difficulties in selecting the correct transfer velocity as this is very site specific (Raymond and Cole, 2001, Kremer et al., 2003). Additionally, this method does not take the effects of precipitation, surface biofilms, vegetation and penetrative convection into account (Raymond and Cole, 2001, Matthews et al., 2003), often making estimates

inaccurate. In low-wind environments, such as in ditches surrounded by reeds, these parameters are even more important in determining gas exchange (Matthews et al., 2003). Conversely, floating flux chambers are able to take vegetation into account when measuring evasion rates. Floating flux chambers use the same basic principal as any static flux chamber, the exchange of gas occurs within a restricted space that can be monitored over a specific time period, allowing for a linear change in concentration to calculate a flux. There are a number of disadvantages with using floating chambers, including: (i) difficulty of use in rough/windy conditions; (ii) the disruption of the processes that they seek to measure, due to the chamber reducing wind over the surface water-atmosphere boundary; (iii) the creation of a microenvironment within the chamber; (iv) pressure differences between the headspace and the atmosphere altering evasion ratios; (v) alterations to the concentration gradient between the surface boundary; and (vi) the movement of the chamber on the water's surface altering evasion rates. Floating flux chambers are, however, the favoured method of calculating evasion rates in low-wind environments due to their low cost, ease of use, rapid response to biological changes and high portability (Kremer et al., 2003, Matthews et al., 2003, Vachon et al., 2010). Due to these reasons, floating flux chambers were used at Sutton Fen and Strumpshaw Fen.

4.2.5.1 Floating flux chamber design

In addition to the design considerations of a static flux chamber (section 4.2.1), the means of chamber floatation need to be determined. In previous studies (Billett and Moore, 2008, Billett and Garnett, 2010, Dinsmore et al., 2010), a large lip around the chamber has been used, along with the gas headspace, to float the chamber. Although this method is rather simple in design construction, it can be unstable in windy conditions. Furthermore, a study by Matthews et al. (2003) found that chambers that sat flush with the water surface had fluxes three to five times higher than those where the walls extended a couple of centimetres into the water due to artificial, chamber-induced disturbances of the air-water boundary layer. Therefore, it was decided to use a chamber that sat below the water level by a couple of centimetres as this would reduce the artificial, chamber-induced alterations to the air-water boundary and would provide a more realistic flux (Matthews et al., 2003).

The chamber design has been used in a previous study by Stamp (2010). Chambers were made out of 6 mm thick rigid, translucent acrylic plastic (obtained from Aquatics online). Chambers were 22.6 x 25.7 cm (width x height) in cross-section and had a basal

area and volume of 0.11 m^2 and 0.028 m^3 when deployed with a 2 cm lip under the water's surface (Stamp, 2010). Chambers were floated using six air-filled sealable bags (Figure 33) that were attached to the chamber rather than foam, as used in Matthews et al. (2003), so as not to alter the basal area of the chamber. Four holes had been drilled into the chamber for a balloon to compensate for pressure changes within the headspace, a probe to measure pressure, humidity and temperature (Commeter C4141, stated manufacturer's accuracy of ± 0.4 °C and ± 0.01 kPa) fitted to a 31 mm base-diameter rubber bung (Fisher Scientific), an inlet and an outlet for an IRGA using three-way stopcocks (Cole Palmer) and a 1.5 m length of tygon tubing (3.2 mm inner diameter (i.d.)) to allow for headspace sampling. Each chamber had a removable, reflective cover made from reflective fibre-reinforced foil as in Stamp (2010). During sampling, a fan was attached to the chamber interior to encourage mixing of air within the headspace. Throughout the summer months, ice packs were fixed to the interior of the chamber to prevent solar irradiation altering flux rates. Chambers were tested in the laboratory for gas tightness in February 2012 and regularly throughout the sampling period.

Figure 33 Deployed floating chamber on a ditch at Sutton Fen

4.2.5.2 Taking floating flux measurements

Sampling took place during the same sampling period as in section 4.2.2, using the same sampling protocol (section 4.2.2). Samples were analysed using GC-FID and the same analysis protocol as in section 4.2.3.

4.2.6 Flux calculations

CO_2 and CH_4 fluxes (mg CO_2/CH_4 m^{-2} h^{-1}) were calculated using a linear regression and were based on the equations (Eq. 17) found in Denmead (2008). Non-linear responses were not used to calculate gas fluxes as thought to be caused by an ebullition event (Altor and Mitsch, 2006). Where removing one sample from the response resulted in a linear response (Figure 34), the sample was removed from the regression as it was probably due to a poorly mixed headspace (Altor and Mitsch, 2006). To calculate a flux, the following measurements are required: temperature and pressure of the enclosed air (noted at each sampling point), gas concentration of the headspace samples being used in the linear regression and the volume of the chamber (including the collar above the peat surface, noted at the start of the run).

To calculate a CO_2 or CH_4 flux, the following equations (Eq. 17) are applied to each gas sample used for the linear regression. Firstly the volume of gas within the flux chamber was calculated using the following equation:

$$V_{field} = \left[C_{gas} \cdot 10^{-6}\right] \cdot V_{chamber} \qquad \text{Eq. 17a}$$

where V_{field} is the volume of gas in the flux chamber at the time of headspace sampling (L), C_{gas} is the concentration of headspace gas (ppm), 10^{-6} is the conversion factor for ppm to L and $V_{chamber}$ is the volume of the flux chamber (L).

V_{field} is then adjusted using the Ideal Gas Equation:

$$V_{STP} = V_{field} \cdot \left(\frac{P_f}{T_f}\right) \cdot \left(\frac{T_{STP}}{P_{STP}}\right) \qquad \text{Eq. 17b}$$

where V_{STP} is the volume of gas in the chamber at standard temperature and pressure (STP; L), P_f and T_f are the headspace barometric pressure and temperature at the time of sampling, respectively, and T_{STP} and P_{STP} are 273.15 K and 100 kPa, respectively. The number of moles of gas (Mol_{gas}) in the flux chamber were calculated by dividing the

volume of gas at STP (V_{STP}) by the volume of one mole of ideal gas (22.7 L mol^{-1}; Eq. 17c).

$$Mol_{gas} = \frac{V_{STP}}{22.7} \quad \text{Eq. 17c}$$

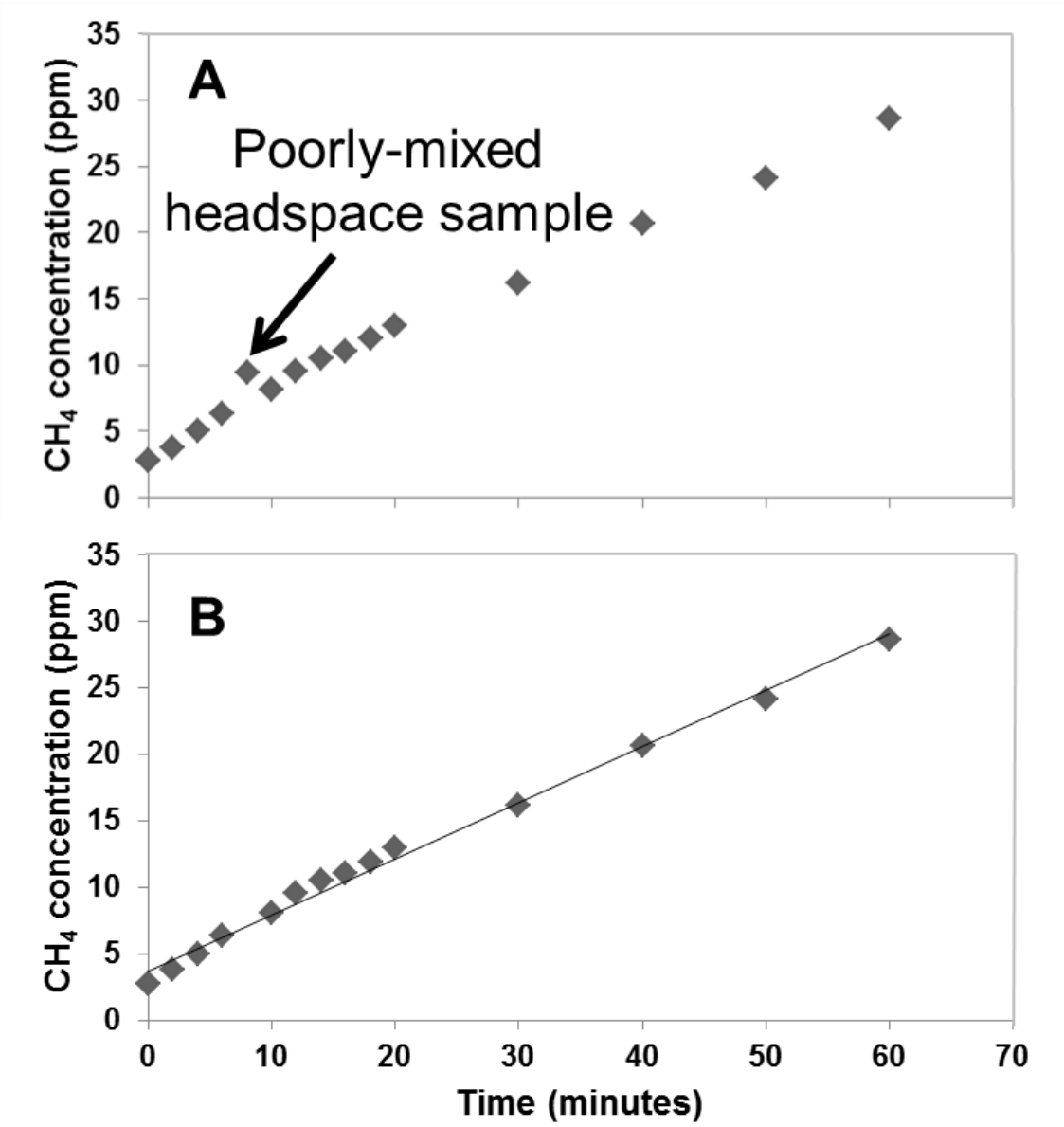


Figure 34 Example of a poorly-mixed headspace sample (A) and its removal along a regression to achieve linearity (B).

Finally, the hourly gas flux rate per square meter per hour was calculated using the following:

$$G_f = \left[\frac{(Mol_{gas+1} - Mol_{gas})}{((t_f - t_i)\cdot 3600)\cdot A}\right] M_{gas} \qquad \text{Eq. 17d}$$

where G_f is the hourly rate of gas flux to the atmosphere (mg CO_2/CH_4 m^{-2} h^{-1}), $[Mol_{gas+1} - Mol_{gas}]$ is the difference in Mol_{gas} between the start and end of sampling, $t_f - t_i$ is the time interval between the first and last headspace samples (seconds), 3600 is the number of seconds in an hour, *A* is the surface area of the collar (m^2) and M_{gas} is the mass of one mole of CO_2 or CH_4 (44.01 and 16.04 g mol^{-1}, respectively).

4.2.6.1 Non-linear fen and ditch CH_4 responses.

A number of non-linear CH_4 responses were observed in the fen and ditch data during the 16 month sampling period (Figure 35). A number of these responses can be attributed to different mechanisms, including an ebullition event causing a step change in a response (Figure 35D) or a steady ebullition event saturating the headspace (Figure 35B), or an unmixed headspace sample (Figure 35E). Other responses, such as Figure 35A, C and F needed to be investigated to ascertain whether they were due to an observer effect.

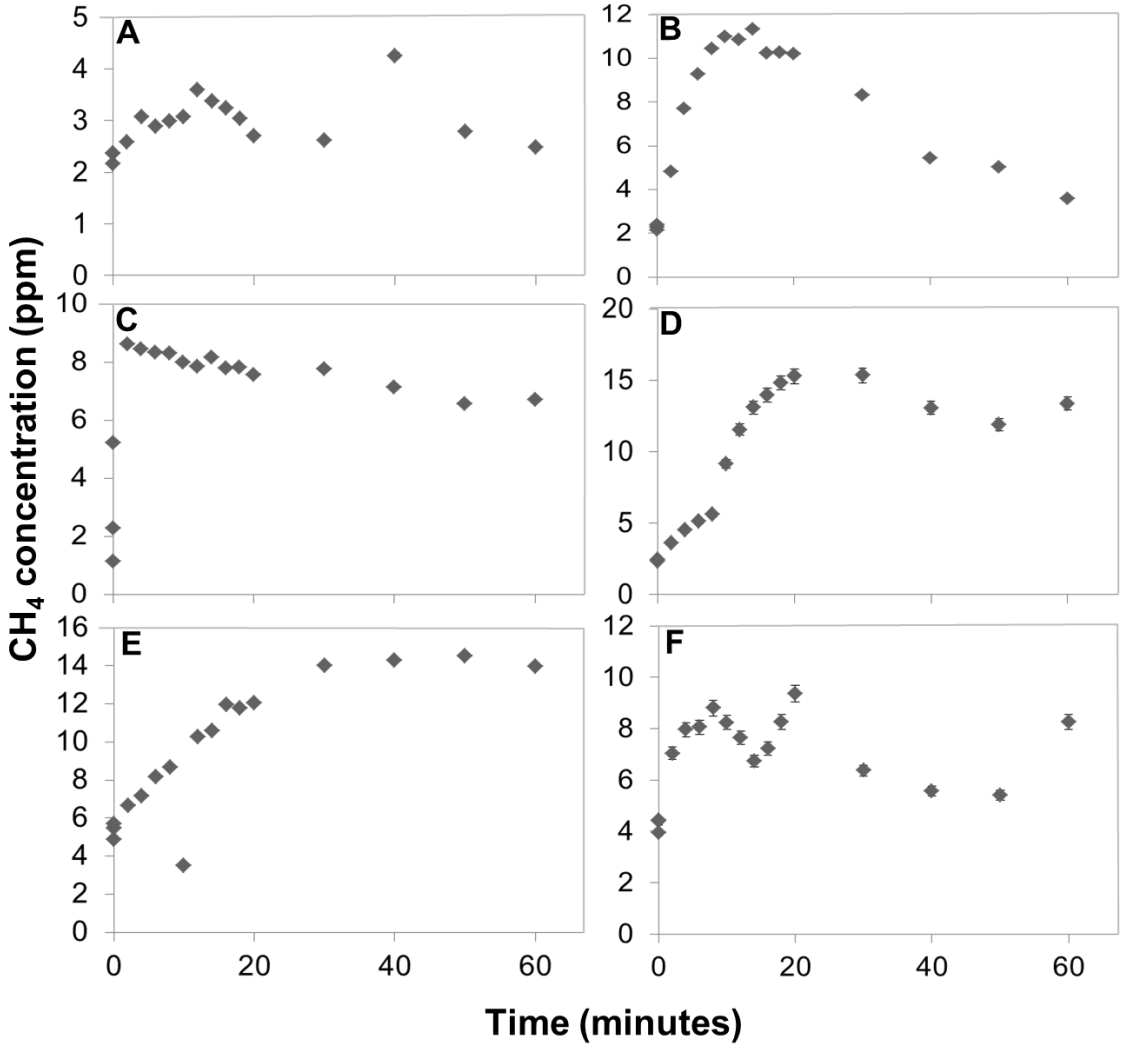


Figure 35 Examples of non-linear CH_4 responses observed during the 16 month sampling period.

To establish if these non-linear fluxes were due to observer induced response, a number of tests were undertaken on 2nd June 2013 at Sutton Fen using a fast methane analyser (FMA; Los Gatos Research Ultraportable Greenhouse Gas Analyser; precision of 0.6 ppb and 100 ppb for CH_4 and CO_2, respectively; ran at 1 Hz) in collaboration with Dr Sophie Green of the University of Leeds. Two different types of tests were undertaken: A) a long term test of 1 hour to establish CH_4 patterns without disturbance and B) a shorter test with physical disturbances to attribute patterns in CH_4 response to disturbances. Test A was undertaken on collars 2 to 4 at Sutton Fen, as these collars had not been syringe sampled prior to the test. The test was conducted under light conditions and work was kept to a minimum in close vicinity to the collars to minimise disturbance (i.e. from shroud placement) during the test.

Results from test A show non-linear responses over the sampling period for all three collars (Figure 36) without observer disturbances. The response for collar 2 (Figure 36A) shows a “humped” increase in CH_4 concentration over time. This non-linear response is not caused by chamber leakage, as CO_2 concentrations within the headspace (Figure 37) do not follow the same pattern. Furthermore, the response is not a function of alterations in PAR, as this too would show in CO_2 concentrations. Figure 35B shows a steady ebullition event saturating the chamber headspace and resulting in a decrease in concentration due to the greater concentration of CH_4 in the headspace than the peat substrate. Figure 36C also shows a steady initial increase in CH_4, which may be caused by a steady ebullition event. Both of the responses for Figure 36B and C may be due to the weight of the chamber being deployed, causing an artificial change in pressure and resulting in an ebullition event. To test this hypothesis, disturbance tests (test B) were under taken to attribute the CH_4 response to the type of disturbance.

Test B was undertaken on collar 5 and 6 at Sutton Fen for 15 minute periods (Figure 38). During this time, 3 types of disturbances were simulated: 1) syringe sample collection, where no sample was taken but the chamber was approached and the action of taking a sample (including the pumping and purging of the sample tubing; section 4.2.2) was undertaken; 2) walking around the chamber in close proximity; and 3) pressing lightly on the top of the chamber to simulate the chamber being placed on the collar.

Test B results (Figure 38) did not show that syringe sampling and walking around the chamber altered CH_4 responses. Even simulated heavy trampling around the chambers did not alter responses. There is a possibility that chamber deployment may induce ebullition events, as seen in collar 5 (Figure 38A). However, this was not observed in collar 6 (Figure 38B) for each of the chamber deployments, suggesting that it may only occur if the area around the collar is primed with CH_4 gas bubbles. Therefore, responses that show the occurrence of ebullition at the start of the run (such as Figure 37B and C) were disregarded. As for the non-linear responses observed in Figure 36, more research needs to be done to fully establish the cause of these types of responses.

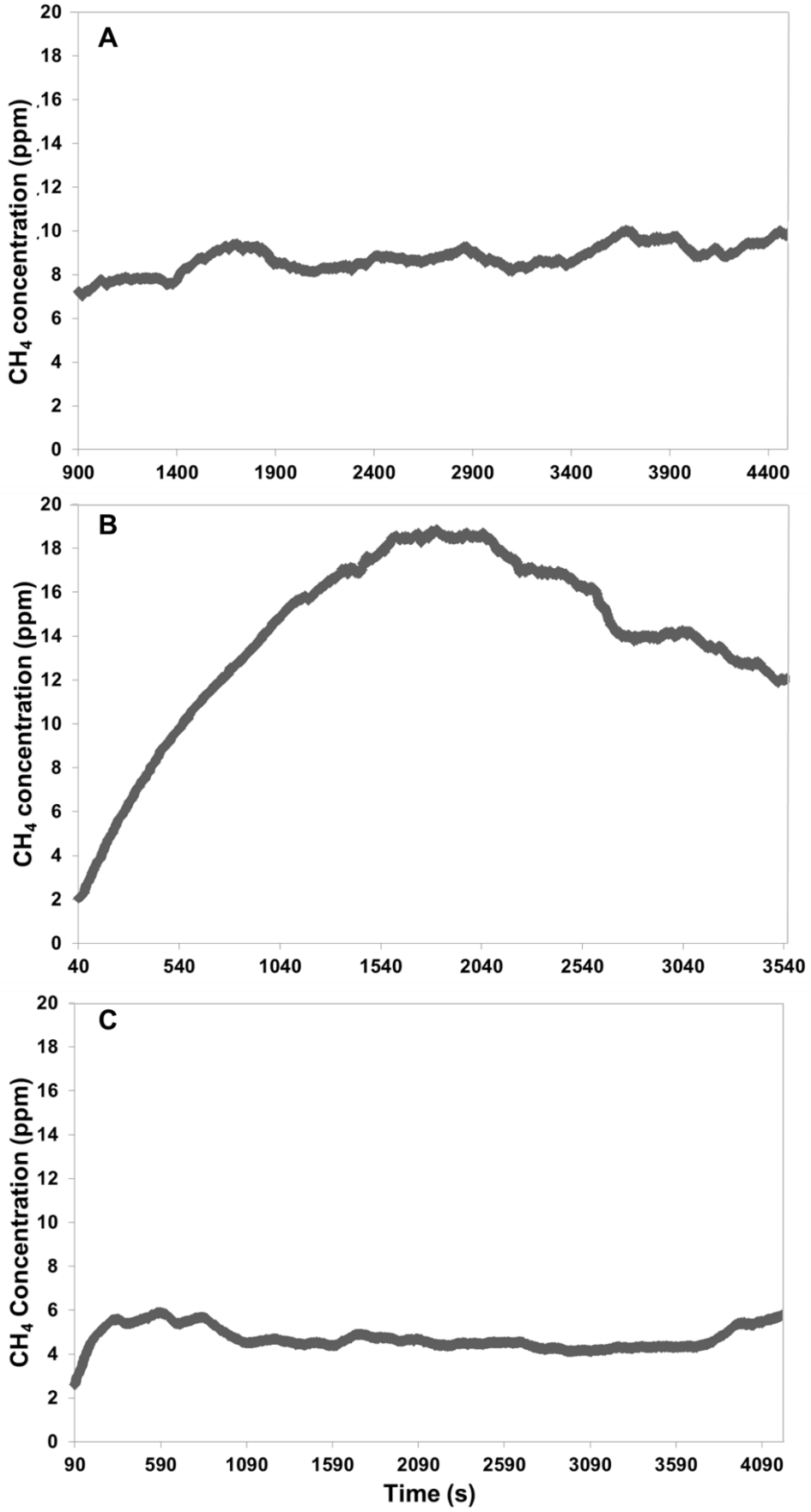


Figure 36 Results from long-term FMA test to establish CH_4 patterns without physical disturbance for collars 2 (A), 3 (B) and 4 (C).

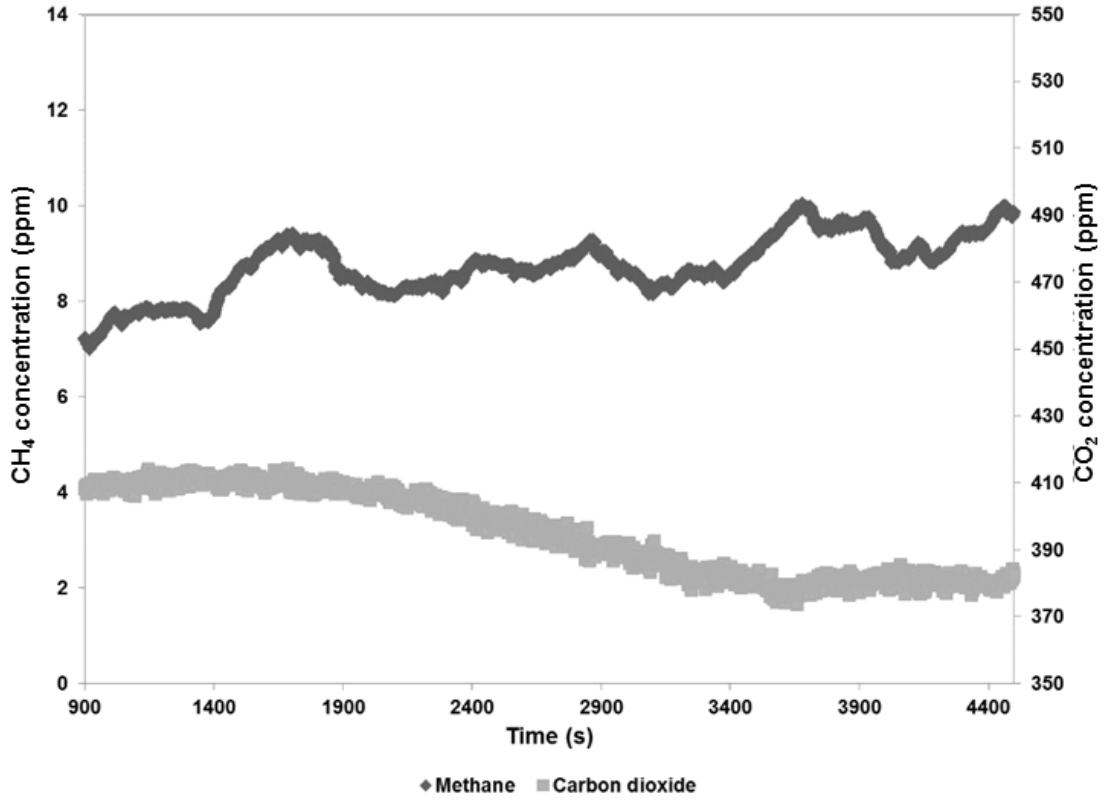


Figure 37 Collar 2 CH_4 and CO_2 concentrations from long-term FMA test without physical disturbances.

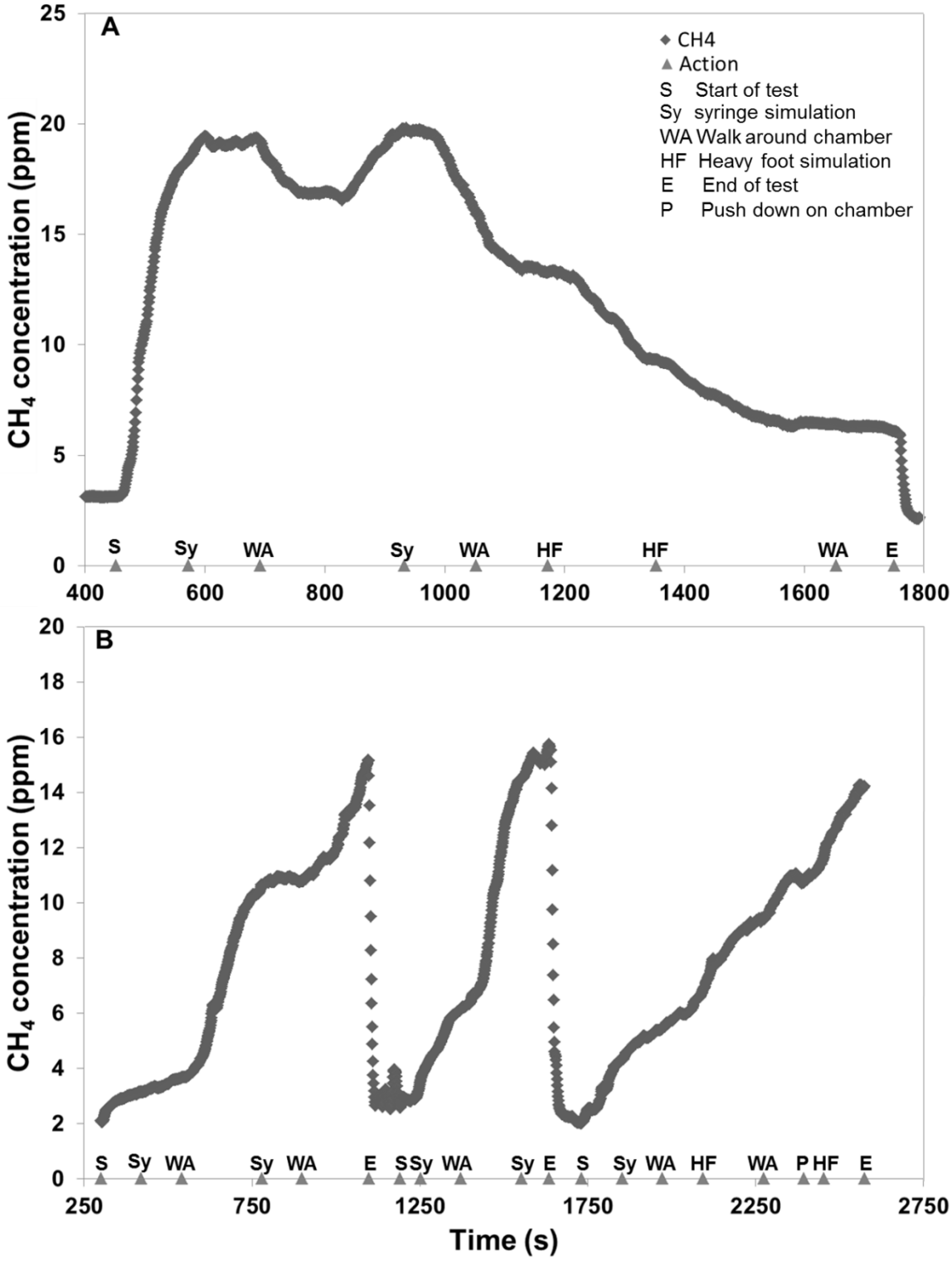


Figure 38 Results from short-term disturbance FMA test to attribute CH_4 patterns to physical disturbances at collars 5 (A) and 6 (B).

4.2.7 Controlling factors modelling

To ascertain what environmental variables control C dynamics in floodplain fens, regression analysis was used as it is a simple, commonly used modelling approach to

derive controlling factors on GPP, R_{eco} and CH_4 fluxes (Audet et al., 2013a, Audet et al., 2013b). Insufficient data to parameterise individual collars separately led to the use of mixed-effects models being used to investigate controlling factors on GPP, R_{eco} and CH_4. Mixed-effects models allow for variation in response variables to be accounted for using fixed and random effects (Crawley, 2012). Fixed effects influence only the mean of the dependent variable, accounting for differences in fluxes between sites (Figure 39A).

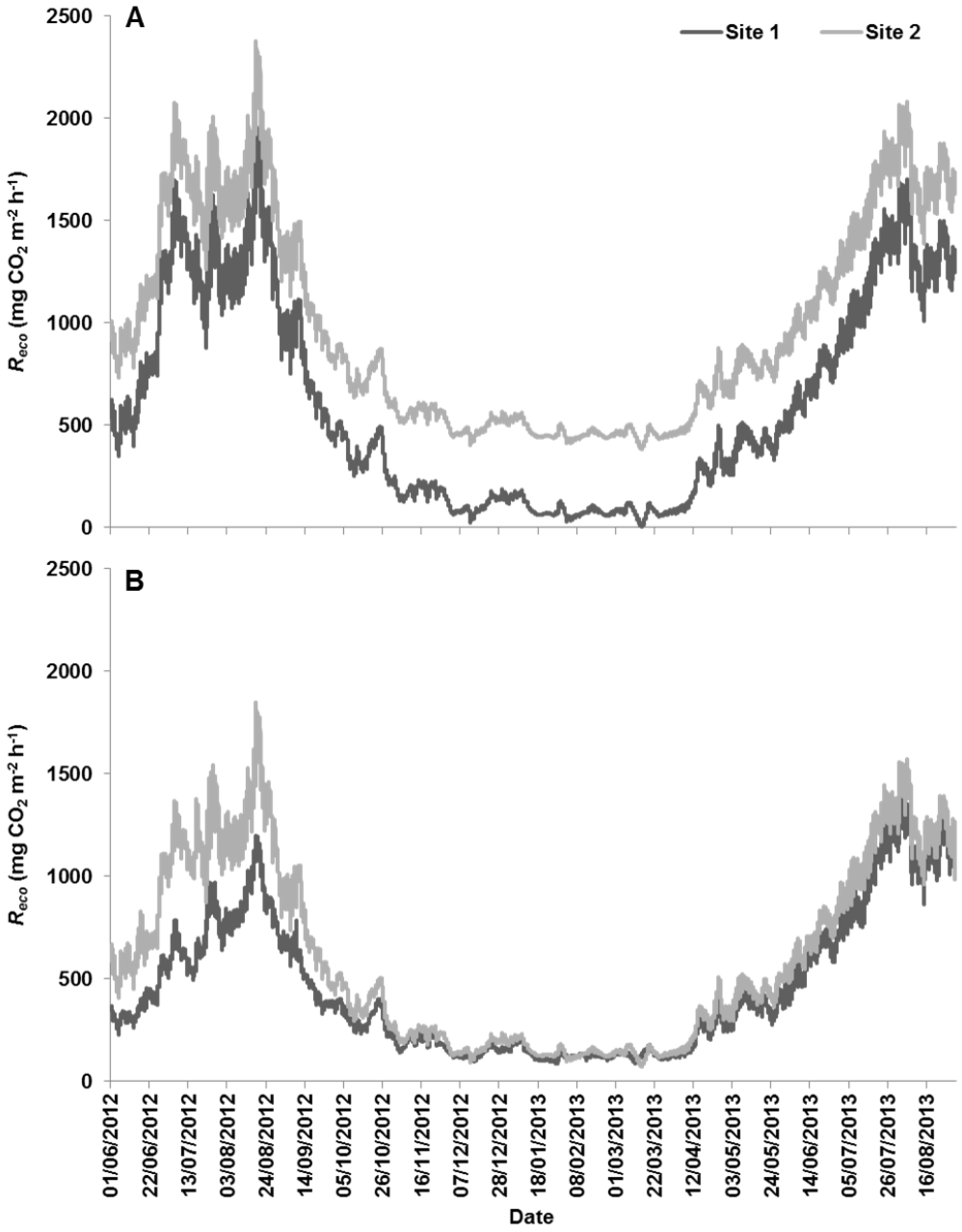


Figure 39 Differences in fixed effects (A; alters mean but not variation between collars) and random effects (B; takes variation in collar into account) on an entire equation for simulated R_{eco} reconstruction.

Meanwhile, a random effect influences the variance of the dependent variable (Crawley, 2012) or as in the case for this research, the variation in fluxes between collars (random effect on entire equation Figure 39B, on the slope and intercept Figure 40). The variation between collars can be captured either on all parameters (Figure 40) or on specific parameters. For example, a random effect on the slope parameter for temperature would show that the response to temperature differs among collars.

In order to create an over parameterised mixed-effects general linear model to investigate GPP, R_{eco} and CH_4 controlling factors, independent variables listed in Table 24 (variables sourced from the literature) were normalised and standardised using Eq. 18. Independent variables were assessed for collinearity, removing the weakest correlation with the dependent variable where collinearity existed. Porewater physicochemistry from the 16 month sampling period was also included in the shortlist and results are reported in section 3.3.6.

$$x_{standardised} = \frac{(x - \min(x))}{(\max(x) - \min(x))} \quad \text{Eq. 18}$$

Where $x_{standardised}$ is the standardised variable value, x is the original variable value, $\min(x)$ is the minimum value observed and $\max(x)$ is the maximum value obersved.

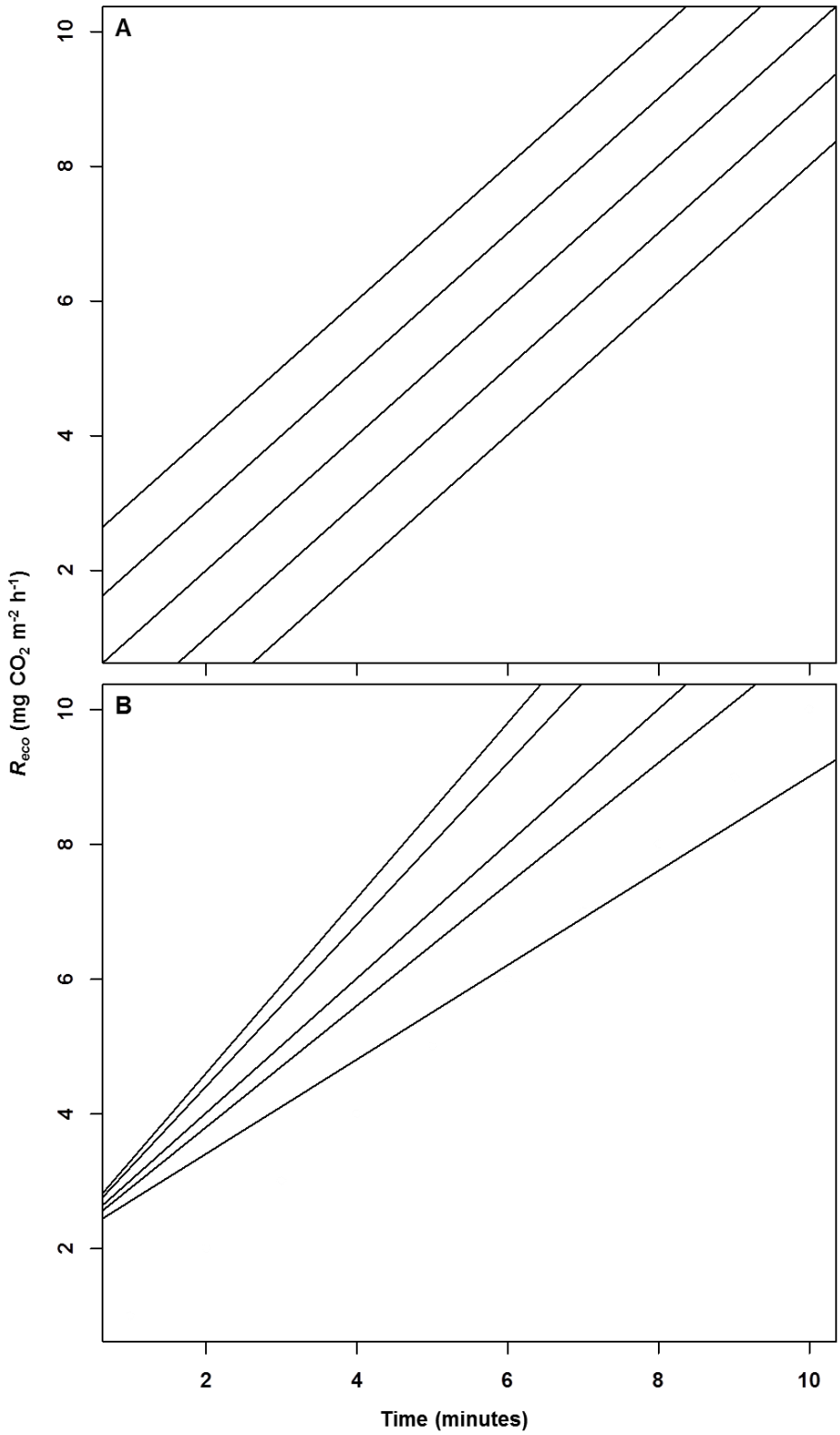


Figure 40 Effects of random effects on the intercept (A) and the slope (B) of an equation.

Table 24 Independent variables for non-linear regressions to investigate relationships between environmental factors and *GPP*, R_{eco} and CH_4.

GPP	R_{eco}	CH_4
Air temperature	Air temperature	Air temperature
Barometric pressure	Barometric pressure	Barometric pressure
Wind speed	Wind speed	Wind speed
PAR	PAR	PAR
VGA	Substrate temperature at 5 cm below peat	VGA
Substrate temperature at 5 cm below peat	Water level	Substrate temperature at 5 cm below peat
Water level	Dissolved porewater CO_2	Water level
Dissolved porewater CO_2	Porewater pH	Dissolved porewater CO_2
Porewater pH	Porewater NO_3^-	Porewater pH
Porewater NO_3^-	Porewater NH_4^+	Porewater NO_3^-
Porewater NH_4^+	Porewater SRP	Porewater NH_4^+
Porewater SRP	Porewater Cl^-	Porewater SRP
Porewater Cl^-	Porewater SO_4^{2-}	Porewater Cl^-
Porewater SO_4^{2-}	Porewater DOC	Porewater SO_4^{2-}
Porewater DOC	Porewater DIC	Porewater DOC
Porewater DIC	Porewater electrical conductivity	Porewater DIC
Porewater electrical conductivity		Porewater electrical conductivity

A final over parameterised model was then built and run with all normalised and standardised independent variables using the lmer function from the lme4 package (Bates et al., 2014). Collar as a random effect was also included in the over-parameterised model. Subset models from the over parameterised global model were then created using the dredge function in the MuMIn package (Barton, 2014). This method allows for the analysis of every single combination of sub models within the global model. Models were then averaged using Akaike weights using the MuMIn package in R (Barton, 2014), a measure of weight of evidence in favour of a model based on a comparison of corrected Akaike information criterion (AICc) with the best model (Burnham and Anderson, 2002). AICc is a means for inter-model comparison, whilst discriminating for the number of independent variables included (Akaike, 1974, Hurvich and Tsai, 1991). AICc was used in preference over Akaike Information Criteria as AICc accounts for a non-negligible bias when the sample size is not so large (Imori et al., 2013). Akaike weights can be used as a means of quantifying relative importance of each parameter, by summing Akaike weights of all the models containing the specific parameter (Burnham and Anderson, 2002, Zuur et al., 2009). If a particular parameter is in all of the top ranking models, then the summed Akaike weight for the parameter will tend towards 1 (Symonds and Moussalli, 2011). However, if the parameter is only in the poorly ranking models, then its weight will trend towards 0 (Symonds and Moussalli, 2011). Parameter weights, as for model weights, can be interpreted as equivalent to the probability that the specific parameter is a component of the best model (Symonds and Moussalli, 2011). Relative importance can then be assessed by ranking he weights, summed across all models, for individual parameters, with larger numbers indicating a parameter is more important than other parameters (Murray and Conner, 2009).

4.2.8 Statistical analysis

All statistical analysis was undertaken in R version 3.1.1 (R Core Team, 2014). Linear regression analysis was used to model PAR from solar irradiance, based on the relationship observed at Sutton Fen. Independent t-tests were used to investigate differences in observed fluxes and water levels between years in the summer months. Linear regressions and independent t-tests were done using the stats package in R (R Core Team, 2014). Pearson product moment correlation was used to investigate the relationship between temperature and methanogenesis, as well as peat temperature between sites using the rcorr function in Hmisc (Harrell and Dupont, 2015). An independent t-test was used to investigate differences in porewater NO_3^-, SRP, Cl^- and SO_4^{2-} concentrations between January and March 2013 at Sutton Fen. All data included in independent t-tests were first subject to checks on normal distribution using the

Shaprio Wilk test (R Core Team, 2014). Independent variables for controlling factors modelling were examined for correlations with the dependent variable using Spearman's rank correlations (rcorr function in Hmisc package (Harrell and Dupont, 2015)). The relative importance of significant controlling factors (H_{4-6}) was investigated using the importance function in the MuMIn package (Barton, 2014).

4.3 Results

4.3.1 Fen CO_2 exchange

Monthly R_{eco} and NEE are presented in Figure 41 from 18th June 2012 to 6th September 2013. NEE follow a seasonal pattern, with greatest uptake during the summer at both sites and small amount of emission during the winter months. NEE varied from -1219 to 448 and -2985 to 772 mg CO_2 m^{-2} h^{-1} for Sutton and Strumpshaw Fen, respectively (negative values indicate net CO_2 uptake and positive fluxes represent a net emission of CO_2). Average monthly NEE over the 16 month period was greater at Strumpshaw (-674 ± 83 mg CO_2 m^{-2} h^{-1}) than at Sutton (-225 ± 43 mg CO_2 m^{-2} h^{-1}). Interestingly, in 2012, Sutton Fen had a greater uptake of CO_2 than at Strumpshaw, yet in 2013 the pattern switched to Strumpshaw having greater uptake of CO_2. This alteration in pattern was not observed in R_{eco}.

R_{eco} followed a seasonal pattern (Figure 41), with greatest emission during the summer months and lesser emission during the autumn and spring months. R_{eco} ranged from 17 to 2295 and 106 to 3420 mg CO_2 m^{-2} h^{-1} for Sutton and Strumpshaw Fen, respectively (positive values indicate CO_2 emission). Average monthly R_{eco} (± 1 S.E.) over the observation period for Sutton and Strumpshaw Fen was 394 ± 46 and 808 ± 96 mg CO_2 m^{-2} h^{-1}, respectively. Apart from August and September 2013, R_{eco} was greater in 2012 than in 2013.

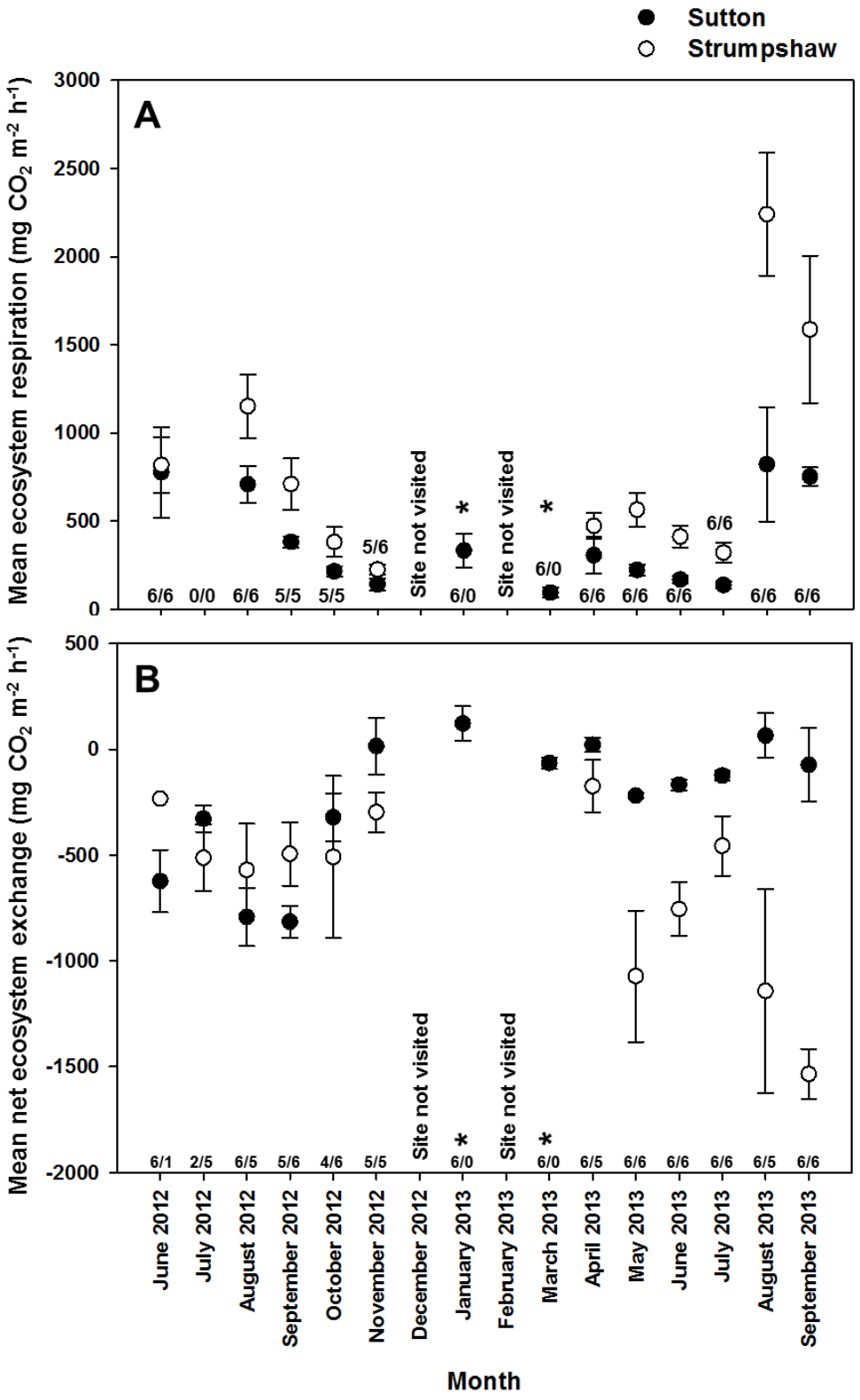


Figure 41 Mean monthly fen R_{eco} (A) and NEE (B) from 18th June 2012 to 6th September 2013 (*n* months sampled = 14 and 12 for Sutton and Strumpshaw, respectively; sites not visited in December 2012 and February 2013) for Sutton and Strumpshaw Fen. Points represent mean values, whilst error bars denote ± 1 standard error and 6/6 represents the number of replicates for Sutton/Strumpshaw. * indicate when only Sutton Fen was sampled.

GPP (R_{eco} - NEE (Chapin et al., 2006)) showed a similar seasonal pattern to NEE (Figure 42; positive fluxes indicate net CO_2 uptake), with the greatest uptake of CO_2 observed in the summer months. GPP was the greatest in summer 2013 for Strumpshaw Fen but in summer 2012 for Sutton Fen. For most of the months sampled at the time sampled (during daylight), GPP was greater than R_{eco}.

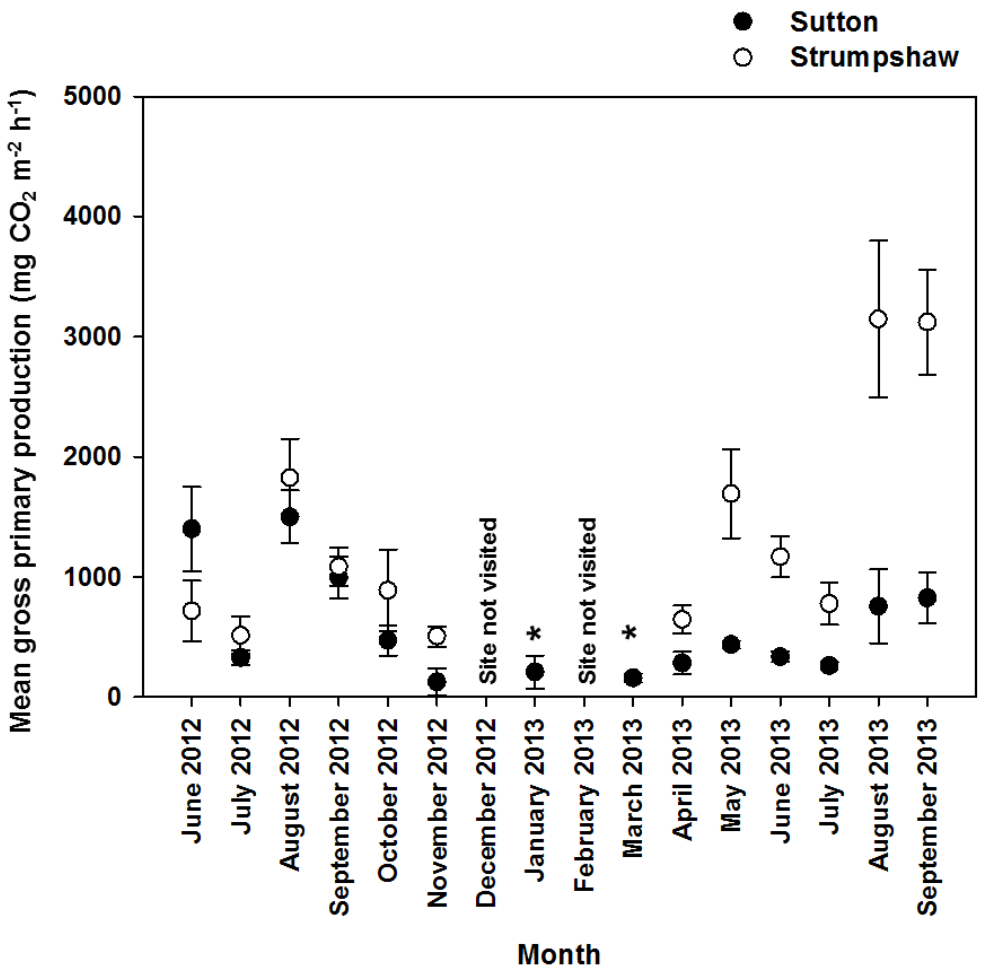


Figure 42 Mean monthly fen GPP (R_{eco} - NEE) from 18th June 2012 to 6th September 2013 (n = 14 and 12 for Sutton and Strumpshaw, respectively; sites not visited in December 2012 and February 2013) for Sutton and Strumpshaw Fen. Points represent mean values and error bars denote ± 1 standard error. * indicate when only Sutton Fen was sampled.

On average, R_{eco} was lowest in spring and autumn and highest in summer (Table 25). Mean monthly R_{eco} was highest in summer 2012 compared to 2013 at both Sutton and Strumpshaw, although the difference between the two years was greater at Sutton (difference between 2012 and 2013 of 367 and 49 mg CO_2 m^{-2} h^{-1} at Sutton and

Strumpshaw Fen, respectively). Autumn and spring fluxes were similar at Sutton (seasonal mean fluxes of 245 and 206 mg CO_2 m^{-2} h^{-1}) and Strumpshaw (seasonal mean fluxes of 422 and 518 mg CO_2 m^{-2} h^{-1}).

Table 25 Summary of seasonal (Summer = June, July and August; Autumn = September, October and November; Winter = December, January and February; and Spring = March, April and May) fen R_{eco} and NEE for Sutton and Strumpshaw Fen from June 2012 to September 2013.

		Ecosystem respiration (mg CO_2 m^{-2} $hour^{-1}$)						
	Season	Mean [1 S.E]	*n*	Median	Min.	Max.	25th percentile	75th percentile
Sutton	Summer 2012	742 [134]	12	681	0	1808	432	1018
	Autumn 2012	245 [32]	15	251	59	485	123	332
	Winter 2012/3	331 [95]	6	345	67	579	105	546
	Spring 2013	206 [41]	18	174	17	661	92	254
	Summer 2013	375 [128]	18	158	64	2296	127	327
Strumpshaw	Summer 2012	1040 [137]	9	1063	532	1820	680	1332
	Autumn 2012	422 [70]	17	297	106	1082	210	716
	Winter 2012/3	N/A	0	N/A	N/A	N/A	N/A	N/A
	Spring 2013	518 [59]	12	474	264	919	373	706
	Summer 2013	990 [242]	18	474	159	3420	279	1580
		Net Ecosystem Exchange (mg CO_2 m^{-2} $hour^{-1}$)						
	Season	Mean [± 1 S.E]	*n*	Median	Min.	Max.	25th percentile	75th percentile
Sutton	Summer 2012	-653 [93]	14	-516	-1219	-208	-362	-996
	Autumn 2012	-378 [114]	14	-405	-994	382	-60	-702
	Winter 2012/3	123 [81]	6	114	-192	383	291	-6.0
	Spring 2013	-80 [29]	17	-76	-241	136	31	-193
	Summer 2013	-75.43 [43]	18	-126	-303	448	-39	-171
Strumpshaw	Summer 2012	-514 [119]	11	-609	-610	205	-151	-824
	Autumn 2012	-441 [141]	17	-401	-2151	772	-261	-588
	Winter 2012/3	N/A	0	N/A	N/A	N/A	N/A	N/A
	Spring 2013	-651 [157]	18	-530	260	2816	-94	-948
	Summer 2013	-721 [157]	18	-530	-2985	0	-277	-991

The greatest uptake of CO_2 occurred within the summer months at both sites (Table 25, with winter 2012 at Sutton Fen changing from sequestering CO_2 to emitting CO_2 (seasonal mean of 122 ± 81 mg CO_2 m^{-2} h^{-1}) at Sutton Fen. Sutton sequestered more CO_2 in summer 2012 (seasonal mean of -654 mg CO_2 m^{-2} h^{-1}), whilst Strumpshaw had a greater seasonal mean in summer 2013 (-721 mg CO_2 m^{-2} h^{-1}). Spring and summer months of 2013 sequestered significantly less CO_2 than summer and autumn 2012. Smallest rates of CO_2 uptake were observed in autumn 2012 at Strumpshaw (seasonal average of -441 ± 141 mg CO_2 m^{-2} h^{-1}). Strumpshaw Fen was not visited during winter months due to time constraints and site access issues.

4.3.2 Fen CO_2 environmental variables

Here environmental variables associated with CO_2 exchange are presented, notably VGA and photosynthetically active radiation (PAR). Air temperature, rainfall and water level data are presented in section 3.3.7, with a summary in Figure 43.

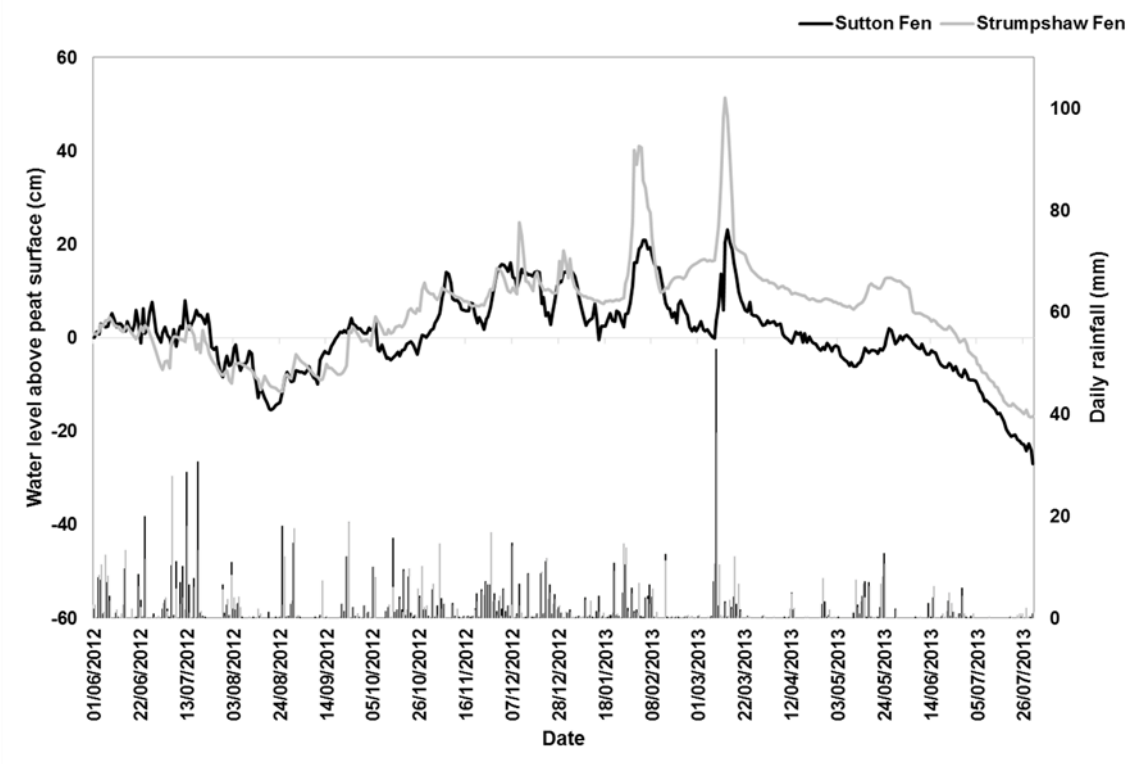


Figure 43 Sutton and Strumpshaw Fen total daily rainfall (mm) and average water level (cm above the peat surface) data from June 2012 to September 2013.

VGA was monitored throughout the GHG sampling period (18th June 2012 to 6th September 2013). Values ranged from 0.03 to 9.8 m^2 m^{-2} for Sutton Fen and 0.06 to 11

m^2 m^{-2} for Strumpshaw Fen (Figure 44). Strumpshaw generally had a higher VGA throughout the year than Sutton. Both sites show a distinct seasonal pattern, with a rapid increase in VGA in spring as a result of increasing atmospheric temperature (Figure 31) and irradiation levels (Wilson et al., 2007a). VGA remained positive throughout the winter months at Sutton due to the evergreen strategy of *J. subnodulosus* and *C. mariscus* (Figure 45) (Wilson et al., 2007b). Strumpshaw was not visited between December 2012 and March 2013 due to land access issues and time constraints. Maximum VGA values were reached later on in the growing season at Strumpshaw, in late summer. The site has a greater *P. australis* abundance (Figure 46), which has a later growing season than *Carex spp. and C. mariscus* (Grime et al., 2007). The onset of senescence was later at Strumpshaw, October-November 2012, than at Sutton Fen (September-October 2012). This difference in vegetation die back is due to differences in plant species composition and abundance, with *P. australis* remaining green at Strumpshaw for much longer than at Sutton (Figure 46). Individual plant species contributions to VGA are shown in Figure 46. Differences in VGA between the two growing seasons were observed at both sites (Figure 44). This is especially noticeable at Sutton Fen, where values were significantly less in 2013 than in 2012.

PAR photosynthetic photon flux density also showed a distinct seasonal pattern (Figure 48), with smaller fluxes in the winter and higher fluxes in the summer. PAR was modelled at Strumpshaw Fen using solar irradiance and the relationship between PAR and solar irradiation at Sutton Fen (Figure 49). Log-transformations on data and nonlinear regressions were used to try to improve the fit between PAR and solar irradiance, but none of these methods significantly improved the fit from Figure 49A.

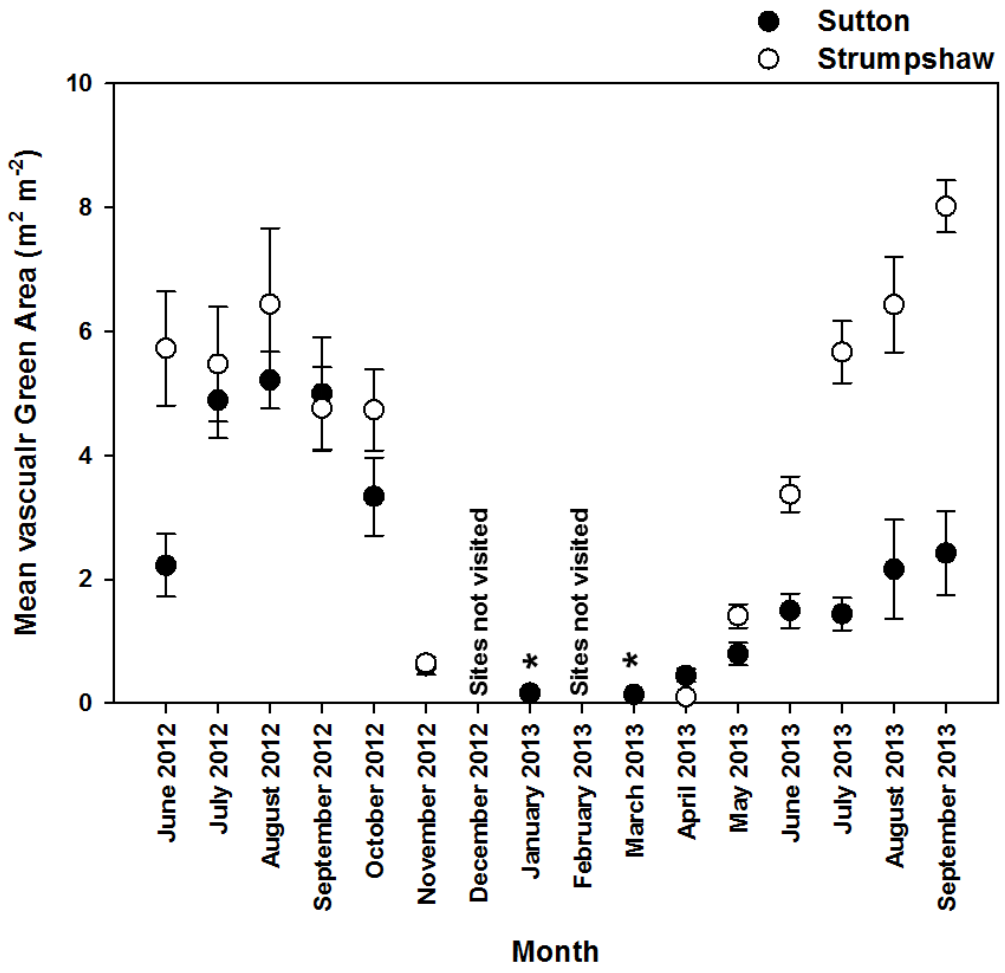


Figure 44 Sutton and Strumpshaw Fen mean VGA values (*n* = 6 per site per month; m^2 m^{-2}) from 18th June 2012 to 6th September 2013. Strumpshaw fen was not visited in January or March 2013. Points represent mean values and error bars denote ± 1 standard error. * indicate when only Sutton Fen was sampled.

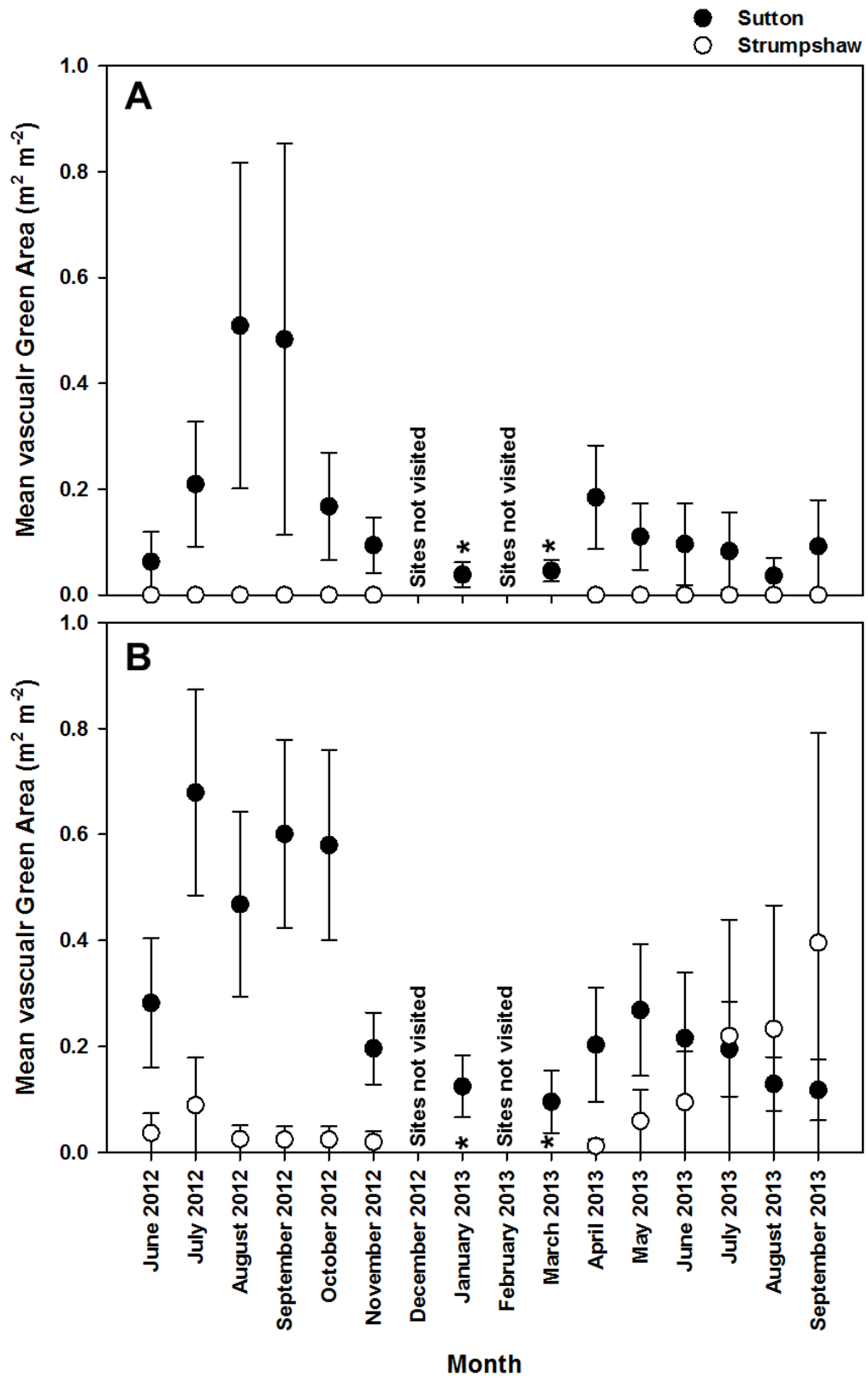


Figure 45 Sutton and Strumpshaw Fen *Cladium mariscus* (A) and *Juncus subnodulosus* (B) mean VGA values (*n* = 6 per site per month; m^2 m^{-2}) from 18th June 2012 to 6th September 2013. Strumpshaw fen was not visited in January or March 2013. Points represent mean values and error bars denote ± 1 standard error. * indicate when only Sutton Fen was sampled.

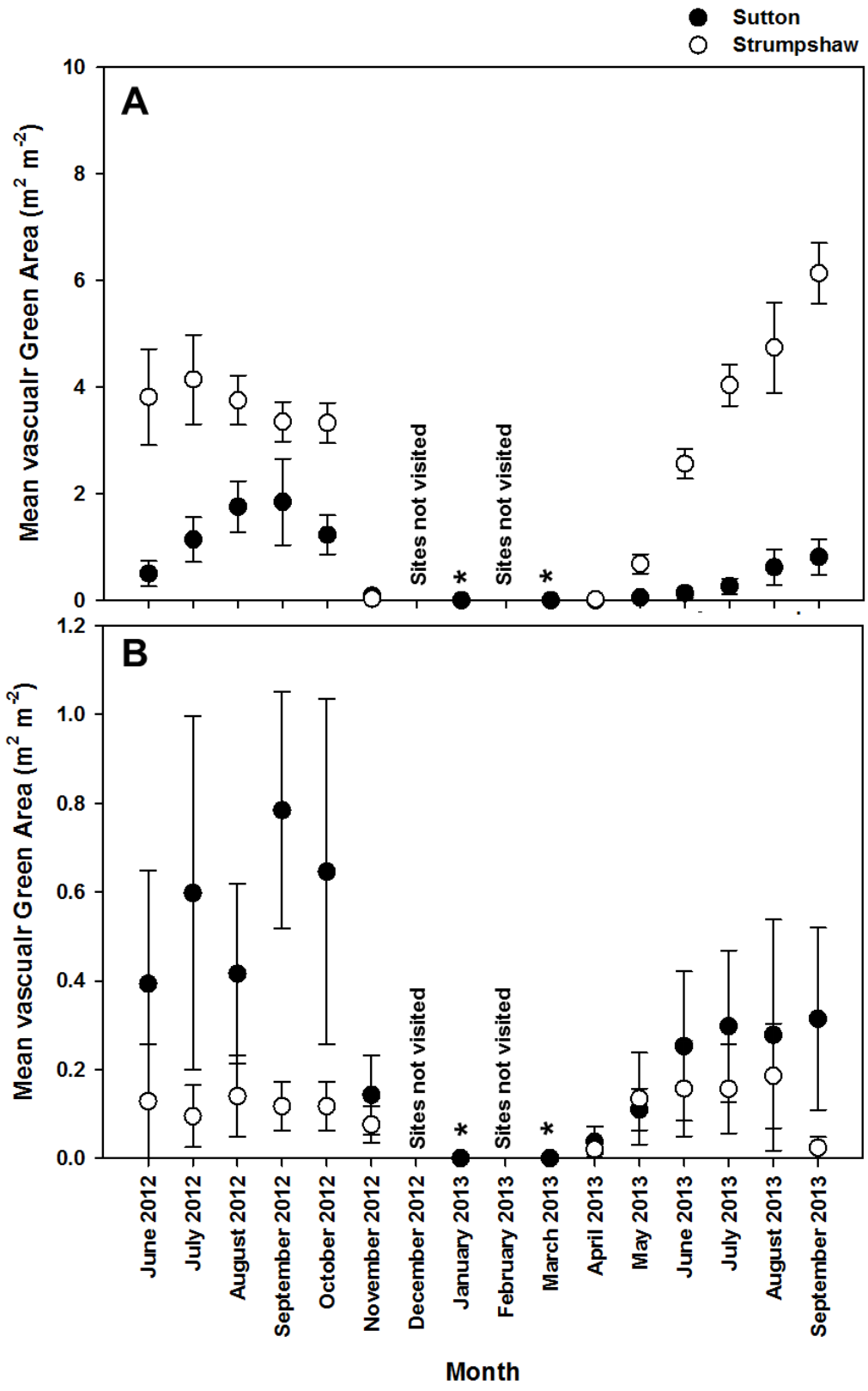


Figure 46 Sutton and Strumpshaw Fen *Phragmites australis* (A) and *Carex spp.* (B) mean VGA values (n = 6 per site per month; m^2 m^{-2}) from 18th June 2012 to 6th September 2013. Strumpshaw fen was not visited in January or March 2013. Points represent mean values and error bars denote ± 1 standard error. * indicate when only Sutton Fen was sampled.

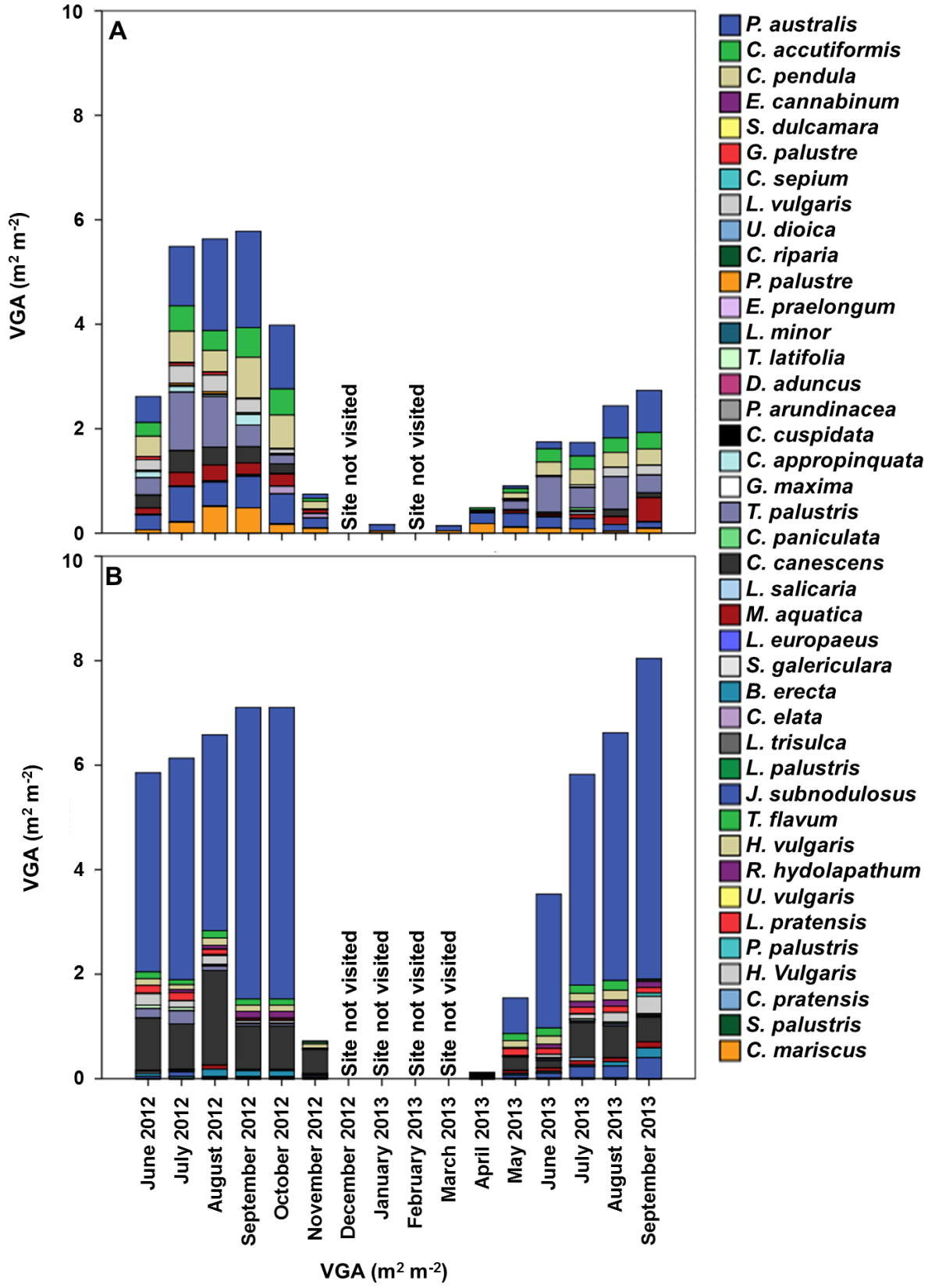


Figure 47 VGA (m^2 m^{-2}; mean per 6 collars) per plant species for Sutton (A) and Strumpshaw Fen (B) from 18th June 2012 to 6th September 2013.

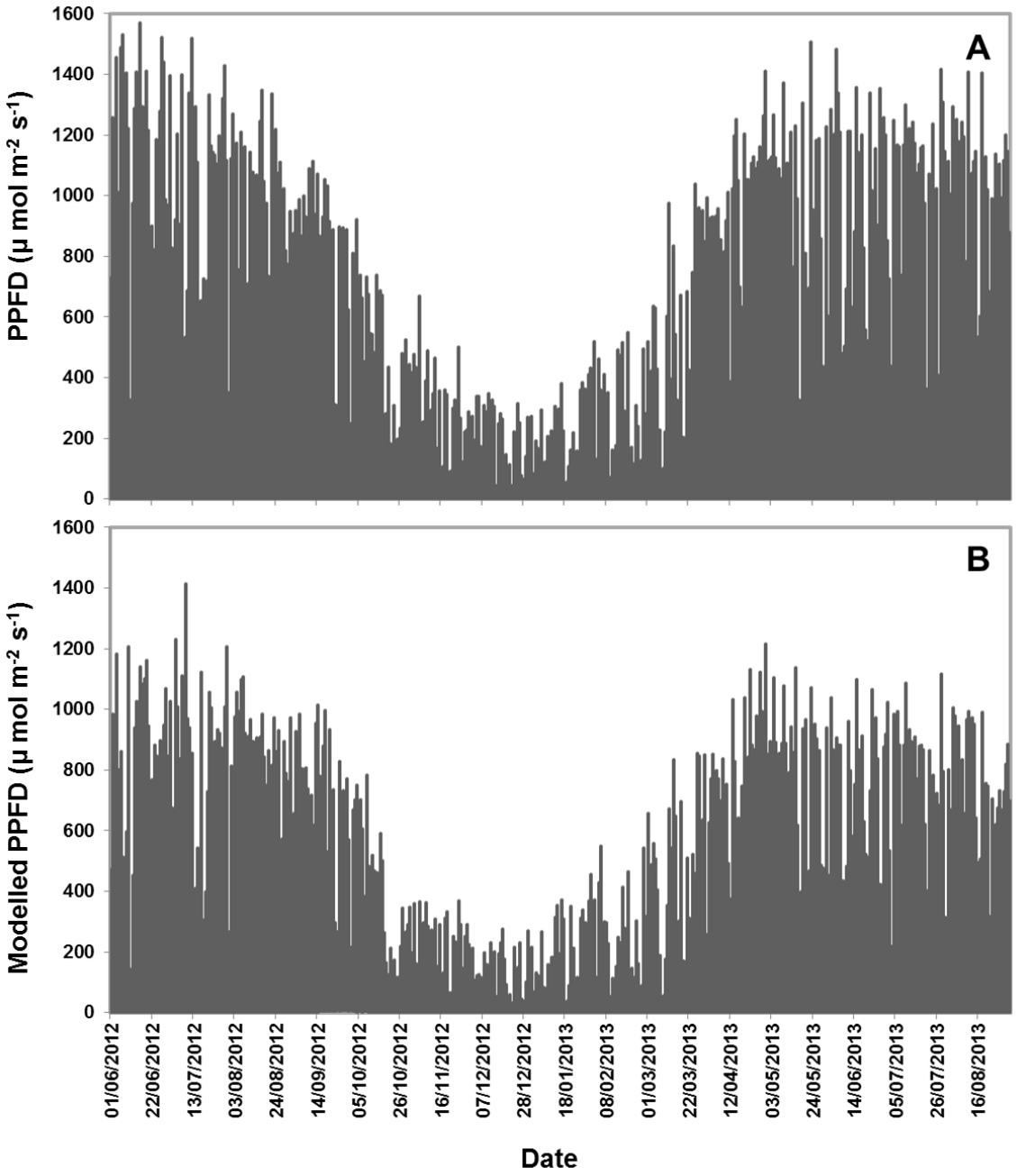


Figure 48 Photosynthetic photon flux density (PPFD) from June 2012 to September 2013 at Sutton Fen (A) and modelled PPFD for Strumpshaw Fen (B), based on the relationship in Figure 49B.

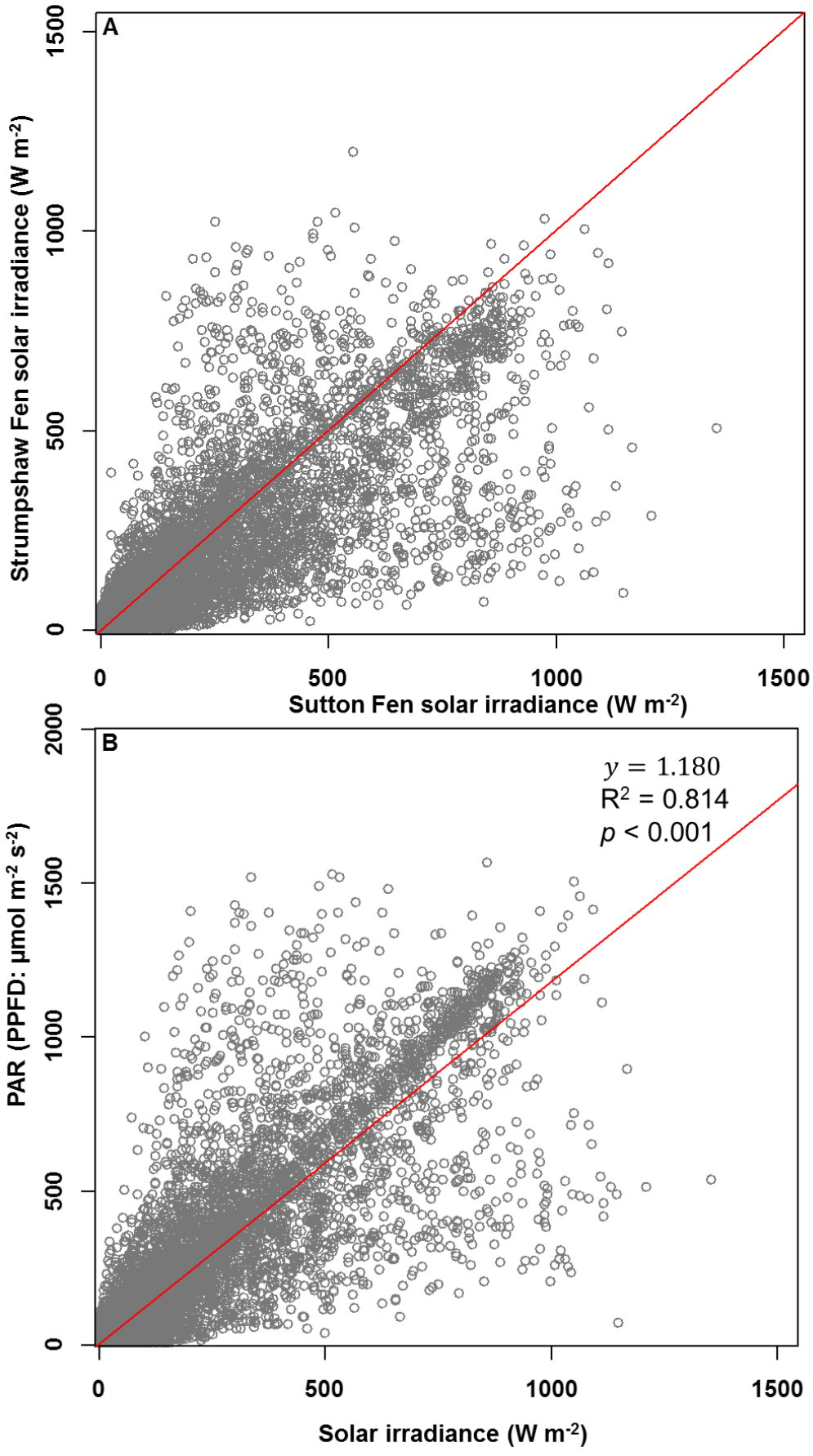


Figure 49 Solar irradiance (W m^{-2}) relationship between Sutton and Strumpshaw Fen (A) and PAR and solar irradiance relationship at Sutton Fen (B).

4.3.3 Ditch CO_2 evasion

Ditch CO_2 evasion, surface water-atmosphere gas transfer, was measured over the same 16 month period as within the fen (18th June 2012 to 6th September 2013; *n* = 14; Figure 50). CO_2 evasion did not follow a distinct pattern at either Sutton and Strumpshaw (*n* = 48 and 41, respectively), with fluxes ranging from -81 to 786 and -71 to 506 mg CO_2 m^{-2} h^{-1}, respectively. August and September 2013 fluxes were significantly greater at both sites than the previous 14 months. The lack of macrophytes within the ditches at both sites meant that ditches were generally a net source of CO_2, apart from April, June and July 2013.

On average, the least amount of CO_2 emitted via R_{eco} was in spring at Sutton and Strumpshaw (Table 26; seasonal mean of 70 ± 13 and 111 ± 48 mg CO_2 m^{-2} h^{-1}, respectively), with fluxes ranging from 39 to 125 and 28 to 246 mg CO_2 m^{-2} h^{-1}, respectively. Despite the best efforts made during sample collection, light could not be completely excluded whilst sampling owing to sunlight penetrating the water column around the floating chamber and a small amount of photosynthetic uptake may have occurred due to phytoplankton and benthic algae. The greatest seasonal mean was summer 2013 for Sutton (124 ± 99 mg CO_2 m^{-2} h^{-1}) and summer 2012 for Strumpshaw (193 ± 37 mg CO_2 m^{-2} h^{-1}).

NEE followed a similar pattern to R_{eco} in that the spring seasonal mean was the smallest mean flux (Table 26; 15 ± 31 and 32 ± 38 mg CO_2 m^{-2} h^{-1} for Sutton and Strumpshaw, respectively), whilst summer months had the greatest seasonal means. Some uptake of CO_2 during the spring and summer months occurred at both Sutton and Strumpshaw Fen (minima of -81 and -71 mg CO_2 m^{-2} h^{-1}, respectively), caused by photosynthesis by phytoplankton and benthic algae, along with cooler temperatures reducing respiration rates. Contrary to R_{eco}, summer 2012 seasonal means were larger than summer 2013 at both sites (2012 seasonal means of 153 ± 9.4 and 152 ± 30 mg CO_2 m^{-2} h^{-1} for Sutton and Strumpshaw, respectively).

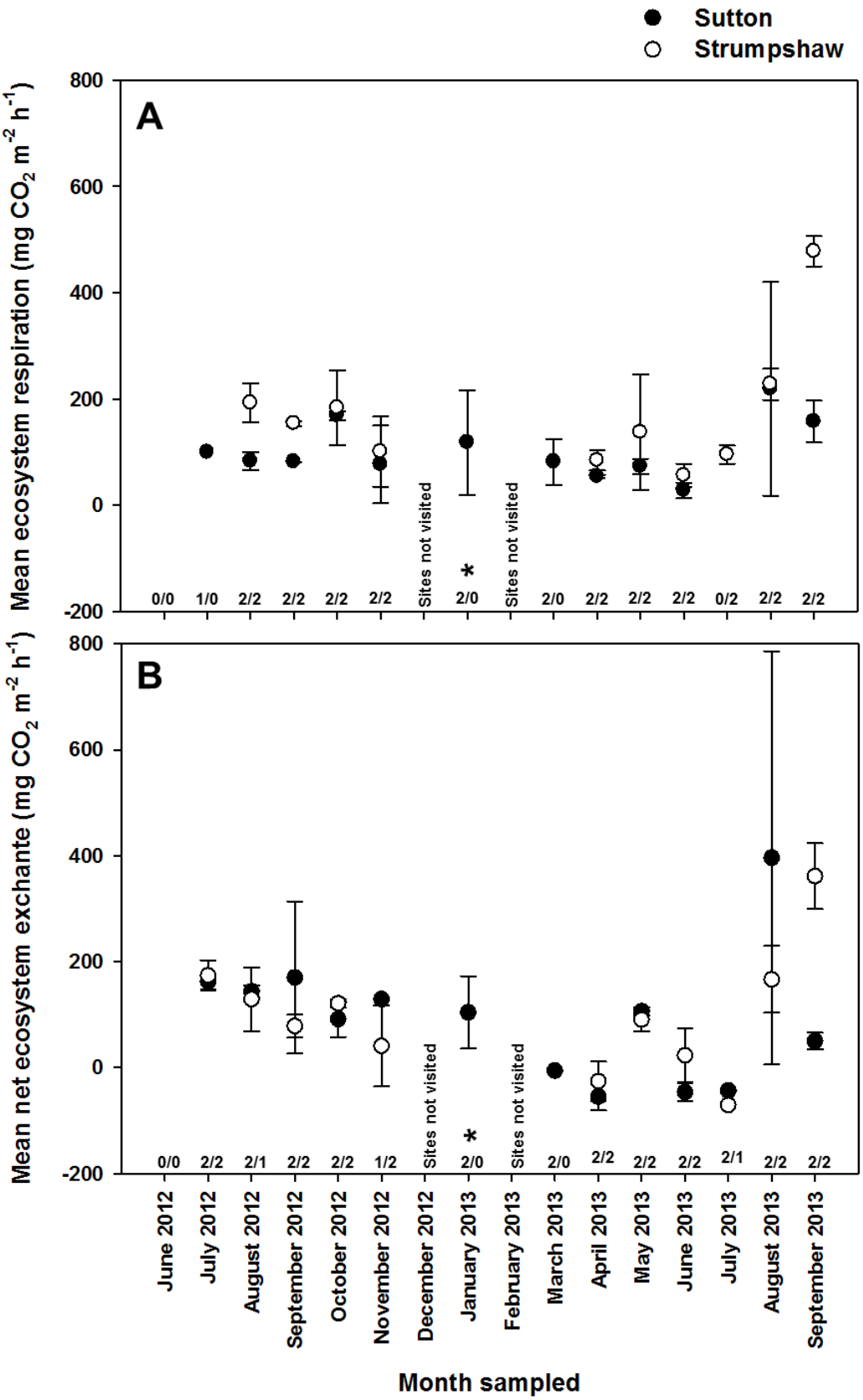


Figure 50 Monthly mean ditch (n = 14) R_{eco} (A) and NEE (B) fluxes from 18th June 2012 to 6th September 2013 at Sutton and Strumpshaw Fens. Points represent mean values, whilst error bars denote ± 1 standard error and 6/6 represents the number of replicates for Sutton/Strumpshaw. * indicate when only Sutton Fen was sampled.

Table 26 Summary of seasonal (Summer = June, July and August; Autumn = September, October and November; Winter = December, January and February; and Spring = March, April and May) R_{eco} and NEE in ditches at Sutton and Strumpshaw Fen (n = 2 per site).

		Ecosystem respiration (mg CO_2 m^{-2} $hour^{-1}$)						
	Season	Mean [± 1 S.E]	*n*	Median	Min.	Max.	25th percentile	75th percentile
Sutton	Summer 2012	89 [± 11]	3	100	66	100	66	N/A
	Autumn 2012	109 [± 27]	6	116	3.7	177	62	164
	Winter 2012/3	118 [± 98]	2	118	20	216	N/A	N/A
	Spring 2013	70 [± 13]	6	58	39	124	48	97
	Summer 2013	124 [± 99]	4	30	13	420	14	326
Strumpshaw	Summer 2012	193 [± 37]	2	193	156	229	N/A	N/A
	Autumn 2012	146 [± 29]	6	154	35	253	94	188
	Winter 2012/3	N/A	0	N/A	N/A	N/A	N/A	N/A
	Spring 2013	111 [± 48]	4	84	28	246	38	210
	Summer 2013	126 [± 35]	6	95	33	257	67	213

		Net Ecosystem Exchange (mg CO_2 m^{-2} $hour^{-1}$)						
	Season	Mean [± 1 S.E]	*n*	Median	Min.	Max.	25th percentile	75th percentile
Sutton	Summer 2012	153 [± 9.4]	4	151	133	178	136	172
	Autumn 2012	131 [± 50]	5	126	27	314	42	222
	Winter 2012/3	102 [± 69]	2	104	36	173	N/A	N/A
	Spring 2013	15 [± 31]	6	-5.8	-81	114	-42	103
	Summer 2013	102 [± 137]	6	-36	-63	786	-49	201
Strumpshaw	Summer 2012	152 [± 30]	4	168	69	203	88	199
	Autumn 2012	80 [± 25]	6	107	-36	129	33	120
	Winter 2012/3	N/A	0	N/A	N/A	N/A	N/A	N/A
	Spring 2013	32 [± 38]	4	40	-63	113	-44	102
	Summer 2013	62 [± 53]	5	74	-71	230	-49	167

4.3.4 Fen CH_4 emissions

CH_4 emissions shown (Figure 51) are calculated only from linear responses (*n* = 51 and 28 for Sutton and Strumpshaw, respectively). Non-linear responses are not shown and are suspected to be caused by ebullition (Section 4.2.6.1 and Figure 51). Fluxes do not follow a clear seasonal pattern as CO_2 (section 4.3.1; Figure 51). Strumpshaw had a greater range in CH_4 emission (0.25 to 134 mg CH_4 m^{-2} h^{-1}) than Sutton (0.17 to 30 mg CH_4 m^{-2} h^{-1}), and a greater mean over the sampling period (12 ± 5.2 mg CH_4 m^{-2} h^{-1} instead of 4.5 ± 0.72 mg CH_4 m^{-2} h^{-1}, respectively).

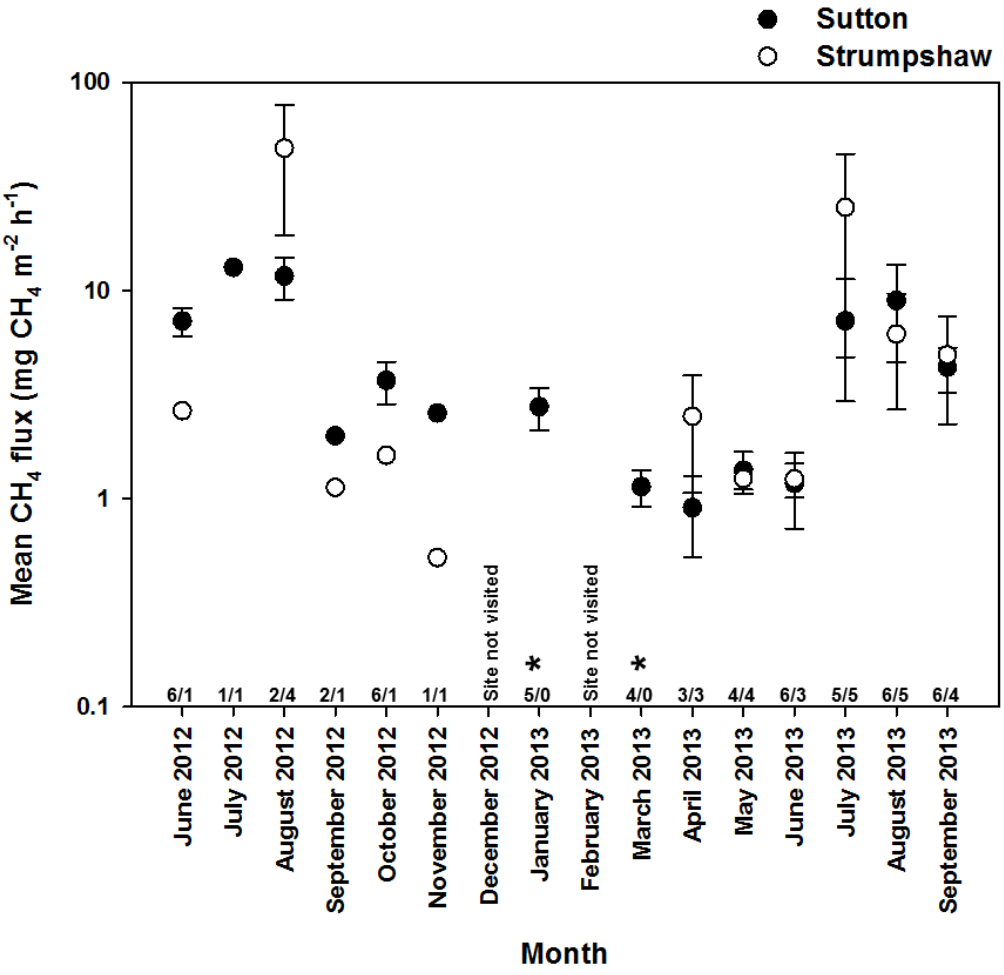


Figure 51 Mean monthly fen CH_4 fluxes (note y axis on logarithmic scale) from 18th June 2012 to 6th September 2013 (*n* months sampled = 14 and 12 for Sutton and Strumpshaw, respectively; sites not visited in December 2012 and February 2013) for Sutton and Strumpshaw Fen. Points represent mean values, whilst error bars denote ± 1 standard error and 6/6 represents the number of replicates for Sutton/Strumpshaw. * indicate when only Sutton Fen was sampled.

On average, summer months (June to August) had the highest CH_4 fluxes at both Sutton and Strumpshaw fens (Table 27). Summer 2012 (June to August 2012) had the greatest mean seasonal flux (8.8 ± 1.2 and 39 ± 25 mg CH_4 m^{-2} h^{-1} for Sutton and Strumpshaw respectively), whilst summer 2013 emitted less CH_4 (mean seasonal flux of 5.7 ± 2.0 and 12 ± 7.9 mg CH_4 m^{-2} h^{-1}). Conversely, summer 2013 had the greatest seasonal maxima (30 mg CH_4 m^{-2} h^{-1}) for Sutton Fen. Spring fluxes were on average the lowest at Sutton Fen, whilst autumn had the lowest seasonal average at Strumpshaw.

Table 27 Summary of seasonal (Summer = June, July and August; Autumn = September, October and November; Winter = December, January and February; and Spring = March, April and May) CH_4 emission for Sutton and Strumpshaw Fen from June 2012 to September 2013.

		CH_4 flux (mg CH_4 m^{-2} $hour^{-1}$)						
	Season	Mean [1 S.E]	*n*	Median	Min.	Max.	25th percentile	75th percentile
Sutton	Summer 2012	8.8 [1.2]	9	9.4	4.0	14	5.1	11
	Autumn 2012	3.2 [0.6]	9	2.6	1.3	7.0	2.0	4.2
	Winter 2012/3	2.8 [0.64]	5	2.2	1.2	4.5	1.5	4.3
	Spring 2013	1.2 [0.17]	11	1.1	0.17	2.0	0.74	1.6
	Summer 2013	5.7 [2.0]	17	2.1	0.48	30	0.78	6.5
Strumpshaw	Summer 2012	39 [25]	5	8.6	2.6	134	5.6	88
	Autumn 2012	1.1 [0.32]	3	1.1	0.5	1.6	0.52	1.1
	Winter 2012/3	N/A	0	N/A	N/A	N/A	N/A	N/A
	Spring 2013	2 [0.6]	7	1.3	0.25	5.1	1.0	2.1
	Summer 2013	12 [7.9]	13	1.6	0.75	105	1.4	8.5

4.3.5 Ditch CH_4 evasion

Ditch CH_4 evasion was measured over the same 16 month period as within the fen (18th June 2012 to 6th September 2013; *n* = 14; Figure 52). In contrast to ditch CO_2 evasion (section 4.3.3), CH_4 evasion from ditches (*n* = 24 at both sites) showed a seasonal pattern (Figure 52; Table 28), with the greatest fluxes during the summer months. Ditch fluxes were significantly different between Sutton and Strumpshaw (Figure 52; annual mean flux of 83 ± 31 and 9.1 ± 3.8 mg CH_4 m^{-2} h^{-1}, respectively), with fluxes ranging from 0.46 to 734 and 0.05 to 89 mg CH_4 m^{-2} h^{-1}, respectively.

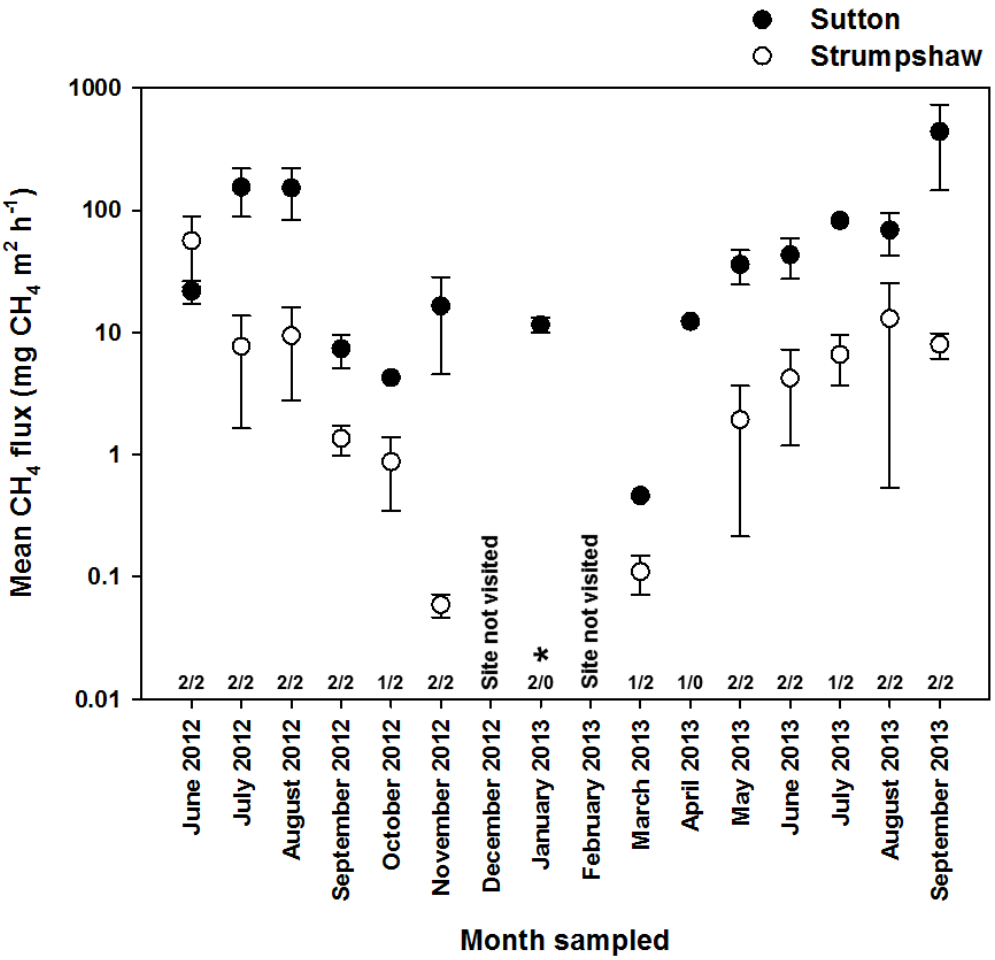


Figure 52 Mean monthly ditch (n = 14) CH_4 evasion from 18th June 2012 to 6th September 2013 at Sutton and Strumpshaw Fen. Points represent mean values, whilst error bars denote ± 1 standard error and 6/6 represents the number of replicates for Sutton/Strumpshaw. * indicate when only Sutton Fen was sampled.

Autumn 2012 seasonal mean for CH_4 (Table 28) was the smallest for both Sutton and Strumpshaw (10 ± 4.6 and 0.76 ± 0.29 mg CH_4 m^{-2} h^{-1}, respectively), whilst summer 2012 had the largest seasonal means (109 ± 37 and 24 ± 13 mg CH_4 m^{-2} h^{-1}). There was a significant difference in mean summer fluxes between 2012 and 2013 for Sutton (109 ± 37 and 61 ± 12 mg CH_4 m^{-2} h^{-1}, respectively) and Strumpshaw (24 ± 13 and 7.9 ± 3.8 mg CH_4 m^{-2} h^{-1}). This difference was more marked at Sutton Fen than at Strumpshaw Fen.

Table 28 Summary of seasonal (Summer = June, July and August; Autumn = September, October and November; Winter = December, January and February; and Spring = March, April and May) CH_4 evasion in ditches at Sutton and Strumpshaw Fen (*n* = 2 per site).

		CH_4 flux (mg CH_4 m^{-2} $hour^{-1}$)						
	Season	Mean [1 S.E]	*n*	Median	Min.	Max.	25th percentile	75th percentile
Sutton	Summer 2012	109 [± 37]	6	86	17	220	24	220
	Autumn 2012	10 [± 4.6]	5	5.1	4.3	29	4.4	19
	Winter 2012/3	12 [± 1.6]	2	12	10	13	N/A	N/A
	Spring 2013	21 [± 10]	4	19	0.46	47	3.4	42
	Summer 2013	61 [± 12]	5	59	27	95	35	89
Strumpshaw	Summer 2012	24 [± 13]	6	15	1.7	89	2.5	40
	Autumn 2012	0.76 [± 0.29]	6	0.66	0.05	1.7	0.07	1.5
	Winter 2012/3	N/A	0	N/A	N/A	N/A	N/A	N/A
	Spring 2013	1.0 [± 0.87]	4	0.18	0.07	3.6	0.09	2.8
	Summer 2013	7.9 [± 3.8]	6	5.5	0.54	25.4	1.0	13

4.3.6 Controlling factors on CO_2 dynamics

Controlling factors on GPP, R_{eco} and CH_4 were established using corrected Akaike Information Criteria (AICc), Akaike weights (defined in section 4.2.7) and the relative importance of each parameter contained with the models. Table 29, 30 and 31 show correlation coefficients for R_{eco}, GPP and CH_4 fluxes, respectively, used to select shortlist of viable variables for each over-parameterised model (Table 32). Relative importance is a measure of how frequently parameters occur in the best fitting models and therefore, they do not sum to one across parameters. Relative importance results are shown in Table 33. The mixed effects modelling of R_{eco}, GPP and CH_4 to calculate the relative importance of independent variables showed that peat and air temperature were controlling factors on R_{eco}, GPP and CH_4 (Table 33). Water level and VGA also played an important role in R_{eco} and GPP. NO_3^- had no controlling factor on GPP, whilst playing a significant role in R_{eco} (relative importance of 83 %). SRP had a controlling factor on both R_{eco} and GPP (relative importance of 100 and 11 %, respectively). PAR played an important role in GPP but not for R_{eco}.

Table 29 Spearman's rank correlation for R_{eco} and select independent variables (air temperature (AT; ˚C), peat temperature (PT; ˚C), water level (WL; cm above peat surface), barometric pressure (Baro; kPa), relative humidity (RH; %), wind speed (WS; m s^{-1}), photosynthetically active radiation (PAR; µmol m^{-2} s^{-1}), vascular green area (VGA; m^2 m^{-2}) porewater dissolved CO_2 (CO_2_Aq; ppm), NO_3^- (mg L^{-1} NO_3^--N), NH_4^+ (mg L^{-1} NH_4^+-N), SRP (mg L^{-1} SRP-P), pH, electrical conductivity (EC; µS cm^{-1}), Fe^{2+} (mg L^{-1}), DOC (mg L^{-1}), DIC (mg L^{-1}), Cl^- (mg L^{-1}) and SO_4^{2-} (mg L^{-1})). * and ** indicate the correlation is significant at the 0.05 and < 0.001 level.

	R_{eco}	AT	PT	WL	Baro	RH	WS	PAR	VGA	CO_2_Aq	pH	SRP	NO_3^-	NH_4^+	EC	Fe^{2+}	DOC	DIC	Cl^-	SO_4^{2-}
R_{eco}																				
AT	**0.59****																			
PT	**0.56****	**0.85****																		
WL	**-0.46****	**-0.71****	**-0.76****																	
Baro	**0.18**	**0.37***	**0.24***	**-0.3****																
RH	**-0.27***	**-0.01**	**0.08**	**0.09***	**0**															
WS	**-0.23***	**0.03**	**0.05**	**-0.01**	**-021**	**-0.03**														
PAR	**0.04**	**0.29***	**0.21**	**-0.1**	**0.42****	**0.05**	**0.29***													
VGA	**0.53****	**0.65****	**0.68****	**-0.49****	**0.45****	**-0.02**	**-0.24***	**0.25***												
CO_2_Aq	**0.14**	**0.06**	**0.06**	**-0.22**	**-0.2**	**-0.18**	**-0.21**	**-0.24***	**-0.04**											
pH	**-0.1**	**-0.18**	**-0.29***	**-0.05**	**-0.13**	**0.03**	**-0.11**	**-0.24***	**-0.1**	**0.13**										
SRP	**0.12**	**-0.06**	**-0.08**	**0.46****	**-0.05**	**-0.18**	**-0.02**	**0.1**	**0.05**	**-0.18**	**-0.23***									
NO_3^-	**-0.14**	**-0.34***	**-0.34***	**0.48****	**-0..24***	**0.08**	**-0.09**	**-0.14**	**-0.22**	**-0.17**	**-0.03**	**0.27***								
NH_4^+	**-0.15**	**0.02**	**-0.03**	**0.07**	**-0.06**	**0.18**	**0.11**	**-0.05**	**-0.18**	**-0.17**	**-0.14**	**-0.01**	**0.15**							
EC	**0.42****	**0.41****	**0.46****	**-0.16**	**0.06**	**-0.09**	**-0.09**	**0.12**	**0.53****	**-0.16**	**0.01**	**0.37***	**-0.16**	**-0.2**						
Fe^{2+}	**-0.19**	**-0.2**	**-0.2**	**-0.01**	**0.12**	**0.01**	**-0.13**	**-0.1**	**-0.21**	**0.13**	**0.06**	**-0.14**	**-0.06**	**0.01**	**-0.5****					
DOC	**-0.46****	**-0.29***	**-0.35**	**0.41****	**-0.18**	**0.28***	**0.01**	**0**	**-0.17**	**0.01**	**0.14**	**-0.05**	**0.29***	**0.08**	**-0.22**	**0.06**				
DIC	**-0.29***	**-0.48****	**-0.6****	**0.69****	**-0.22**	**-0.07**	**0.11**	**0.06**	**-0.42****	**0.01**	**-0.02**	**0.34***	**0.3***	**-0.04**	**-0.23**	**-0.01**	**0.24**			
Cl^-	**0.52****	**0.41****	**0.49***	**-0.14**	**0.06**	**-0.04**	**0.02**	**0.14**	**0.56****	**-0.24***	**-0.06**	**0.35***	**0.05**	**-0.19**	**0.81****	**-0.57****	**-0.24***	**-0.23**		
SO_4^{2-}	**0.26***	**0.16**	**0.19**	**0.01**	**-0.01**	**-0.14**	**0.16**	**0.02**	**0.2**	**-0.35***	**-0.12**	**0.33***	**0.08**	**-0.06**	**0.52****	**-0.5****	**-0.35***	**-0.07**	**0.66****	

Table 30 Spearman's rank correlation for GPP and select independent variables ((air temperature (AT; ˚C), peat temperature (PT; ˚C), water level (WL; cm above peat surface), barometric pressure (Baro; kPa), relative humidity (RH; %), wind speed (WS; m s^{-1}), photosynthetically active radiation (PAR; µmol m^{-2} s^{-1}), vascular green area (VGA; m^2 m^{-2}) porewater dissolved CO_2 (CO_2_Aq; ppm), NO_3^- (mg L^{-1} NO_3^--N), NH_4^+ (mg L^{-1} NH_4^+-N), SRP (mg L^{-1} SRP-P), pH, electrical conductivity (EC; µS cm^{-1}), Fe^{2+} (mg L^{-1}), DOC (mg L^{-1}), DIC (mg L^{-1}), Cl^- (mg L^{-1}) and SO_4^{2-} (mg L^{-1})). * and ** indicate the correlation is significant at the 0.05 and < 0.001 level.

	GPP	AT	PT	WL	Baro	RH	WS	PAR	VGA	CO_2_Aq	pH	SRP	NO_3^-	NH_4^+	EC	Fe^{2+}	DOC	DIC	Cl^-	SO_4^{2-}
GPP																				
AT	**0.56****																			
PT	**0.57****	**0.65****																		
WL	**-0.34***	**-0.54****	**-0.76****																	
Baro	**0.22**	**0.46****	**0.30***	**-0.4****																
RH	**-0.33***	**-0.47****	**-0.14**	**0.11**	**-0.13**															
WS	**-0.26***	**-0.03**	**0.04**	**0.2**	**-0.18**	**-0.12**														
PAR	**0.16**	**0.43****	**0.29***	**-0.17**	**0.33***	**-0.36**	**0.34***													
VGA	**0.67****	**0.62****	**0.68****	**-0.49***	**0.48****	**-0.22***	**-0.24***	**0.19**												
CO_2_Aq	**0.1**	**0.11**	**0.06**	**-0.22**	**-0.12**	**-0.13****	**-0.12**	**-0.15**	**-0.04**											
pH	**-0.24***	**-0.36***	**-0.29***	**-0.05**	**-0.2**	**0.016**	**-0.09**	**-0.21**	**-0.1**	**0.13**										
SRP	**0.28***	**0.04**	**-0.08**	**0.46****	**-0.02**	**-0.15**	**-0.03**	**0.08**	**0.05**	**-0.18**	**-0.23***									
NO_3^-	**-0.17**	**-0.25***	**-0.34***	**0.48****	**-0.33****	**0.15***	**-0.11**	**-0.28**	**-0.22**	**-0.17**	**-0.03**	**0.27***								
NH_4^+	**-0.27**	**-0.02**	**-0.03**	**0.07**	**-0.06**	**0.18**	**0.08**	**-0.09**	**-0.18**	**-0.17**	**-0.14**	**-0.1**	**0.15**							
EC	**0.57****	**0.30***	**0.46****	**-0.16**	**0.04**	**0**	**-0.09**	**0.11**	**0.53****	**-0.16**	**0.01**	**0.37***	**-0.16**	**-0.2***						
Fe^{2+}	**-0.24***	**-0.15**	**-0.2**	**-0.01**	**0.19**	**0**	**-0.12**	**-0.13**	**-0.21**	**0.13**	**0.06**	**-0.14**	**-0.06**	**0.01**	**-0.5****					
DOC	**-0.32***	**-0.18**	**-0.35***	**0.41****	**-0.25***	**0.09***	**0.05**	**0.07**	**-0.17**	**0.01**	**0.14**	**-0.05**	**0.29***	**0.08**	**-0.22**	**0.06**				
DIC	**-0.25***	**-0.33***	**-0.6****	**0.69****	**-0.29***	**-0.09***	**0.16**	**-0.03**	**-0.42****	**0.01**	**-0.02**	**0.34***	**0.3***	**-0.04**	**-0.23**	**-0.01**	**0.24**			
Cl^-	**0.59****	**0.27***	**0.49****	**-0.14**	**0.06**	**0.03**	**-0.01**	**0.1**	**0.56****	**-0.24***	**-0.06**	**0.35***	**0.05**	**-0.19**	**0.81**	**-0.57****	**-0.24***	**-0.23***		
SO_4^{2-}	**0.25***	**0.03**	**0.19**	**0.01**	**0.01**	**0.08**	**0.15**	**-0.02**	**0.2**	**-0.35****	**-0.12**	**0.33***	**0.08**	**-0.06**	**0.52**	**-0.5****	**-0.35****	**-0.07**	**0.66****	

Table 31 Spearman's rank correlation for CH_4 flux and selected independent (air temperature (AT; ˚C), peat temperature (PT; ˚C), water level (WL; cm above peat surface), barometric pressure (Baro; kPa), relative humidity (RH; %), wind speed (WS; m s^{-1}), photosynthetically active radiation (PAR; µmol m^{-2} s^{-1}), vascular green area (VGA; m^2 m^{-2}) porewater dissolved CH_4 (CH_4_Aq; ppm), NO_3^- (mg L^{-1} NO_3^--N), NH_4^+ (mg L^{-1} NH_4^+-N), SRP (mg L^{-1} SRP-P), pH, electrical conductivity (EC; µS cm^{-1}), Fe^{2+} (mg L^{-1}), DOC (mg L^{-1}), DIC (mg L^{-1}), Cl^- (mg L^{-1}) and SO_4^{2-} (mg L^{-1})). * and ** indicate the correlation is significant at the 0.05 and < 0.001 level.

	CH_4	AT	PT	WL	Baro	RH	WS	PAR	VGA	CH_4_Aq	pH	SRP	NO_3^-	NH_4^+	EC	Fe^{2+}	DOC	DIC	Cl^-	SO_4^{2-}
CH_4																				
AT	**0.29***																			
PT	**0.43****	**0.64****																		
WL	**-0.46****	**-0.53****	**-0.76****																	
Baro	**0.2**	**0.51****	**0.3***	**-0.39****																
RH	**0.01**	**-0.5****	**-0.14**	**0.11**	**-0.16**															
WS	**-0.21**	**-0.04**	**0.04**	**0.02**	**-0.18**	**-0.12**														
PAR	**-0.02**	**0.46****	**0.29***	**-0.17**	**0.34***	**-0.36***	**0.34***													
VGA	**0.29**	**0.64****	**0.68****	**-0.49***	**0.49****	**-0.22**	**-0.24***	**0.19**												
CH_4_Aq	**-0.14**	**0.09**	**-0.13**	**0.1**	**-0.16**	**-0.15**	**-0.08**	**-0.09**	**-0.05**											
pH	**-0.12**	**-0.37****	**-0.29***	**-0.05**	**-0.21**	**0.16**	**-0.09**	**-0.21**	**-0.1**	**0.19**										
SRP	**-0.05**	**0.08**	**-0.08**	**0.46****	**-0.01**	**-0.15**	**-0.03**	**0.08**	**0.05**	**0.15**	**-0.23***									
NO_3^-	**0.03**	**-0.29***	**-0.34***	**0.48****	**-0.33***	**0.15**	**-0.11**	**-0.28***	**-0.22**	**0.08**	**-0.03**	**0.27***								
NH_4^+	**0.08**	**-0.08**	**-0.03**	**0.07**	**-0.05**	**0.18**	**0.08**	**-0.09**	**-0.18**	**-0.05**	**-0.14**	**-0.1**	**0.15***							
EC	**0.01**	**0.32***	**0.46****	**-0.16**	**0.05**	**0**	**-0.09**	**0.11**	**0.53****	**0.15**	**0.01**	**0.37**	**-0.16**	**-0.2**						
Fe^{2+}	**0.06**	**-0.15**	**-0.2**	**-0.01**	**0.18**	**0**	**-0.12**	**-0.13**	**-0.21**	**-0.21**	**0.06**	**-0.14**	**-0.06****	**0.01**	**-0.5****					
DOC	**-0.11**	**-0.21**	**-0.35***	**0.41****	**-0.25**	**0.09**	**0.05**	**0.07**	**-0.17**	**0.04**	**0.14**	**-0.05**	**0.29**	**0.08**	**-0.22**	**0.06**				
DIC	**-0.46****	**-0.31****	**-0.6****	**0.69****	**-0.3***	**-0.09**	**0.16**	**-0.03**	**-0.42****	**0.27***	**-0.02**	**0.34**	**0.3***	**-0.04**	**-0.23**	**-0.01**	**0.24***			
Cl^-	**0.08**	**0.29***	**0.49****	**-0.14**	**0.07**	**0.03**	**-0.01**	**0.1**	**-0.56****	**0.04**	**-0.06**	**0.35**	**0.05***	**-0.19**	**0.81****	**-0.57****	**-0.24***	**-0.23**		
SO_4^{2-}	**-0.04**	**0.08**	**0.19**	**0.01**	**0.01**	**0.08**	**0.15**	**-0.02**	**0.2**	**-0.06**	**-0.12**	**0.33**	**0.08***	**0.06**	**0.52****	**-0.5****	**-0.35***	**-0.07**	**0.66****	

Table 32 Independent variables included in R_{eco} and GPP controlling factors models.

R_{eco}	GPP	CH_4
Peat temperature	Air temperature	Peat temperature
Water level	Water level	Water level
Barometric pressure	Barometric pressure	Barometric pressure
VGA	VGA	VGA
Relative humidity	Relative humidity	Relative humidity
Wind speed	PAR	Wind speed
PAR	Dissolved CO_2	PAR
Dissolved CO_2	pH	Dissolved CH_4
pH	Electrical conductivity	pH
Electrical conductivity	SRP	Electrical conductivity
SRP	NO_3^-	SRP
NO_3^-	NH_4^+	NO_3^-
NH_4^+	Fe^{2+}	NH_4^+
Fe^{2+}	Cl^-	Fe^{2+}
DOC	SO_4^{2-}	DOC
DIC		DIC
Cl^-		Cl^-
SO_4^{2-}		SO_4^{2-}

Table 33 Relative importance (R_i), based on the summing of Akaike weights across all models, of each controlling variable on R_{eco}, GPP and CH_4.

R_{eco}		GPP		CH_4	
Parameter	R_i	Parameter	R_i	Parameter	R_i
Peat temperature	1.00	PAR	1.00	Wind speed	0.95
SRP	1.00	Electrical conductivity	1.00	Peat temperature	0.84
VGA	1.00	Relative humidity	1.00	pH	0.34
Water level	1.00	pH	0.90	Electrical conductivity	0.32
Dissolved CO_2	0.96	VGA	0.82	DIC	0.31
DOC	0.96	Air temperature	0.29	Water level	0.18
pH	0.96	Water level	0.27	PAR	0.17
DIC	0.93	Barometric pressure	0.25	NO_3^-	0.10
Barometric pressure	0.92	SRP	0.11	VGA	0.08
NO_3^-	0.83	Wind speed	0.06	Barometric pressure	0.03
Electrical conductivity	0.80	NH_4^+	0.02	Relative humidity	0.03
Fe^{2+}	0.39			SRP	0.03
NH_4^+	0.30			DOC	0.02
				Cl^-	0.01
				NH_4^+	0.01

Results from mixed effects modelling of CH_4 emissions to calculate the relative importance of select independent variables (Table 33) showed that wind speed and peat temperature were significant controlling factors on CH_4 emission (relative importance of 0.95 and 0.84, respectively). Water level and vascular green area (VGA) also played a role in CH_4 emission (relative importance of 0.18 and 0.8, respectively). Photosynthetically active radiation (PAR) played a minor role in CH_4 emission (relative importance of 0.17). NO_3^- and soluble reactive phosphorous (SRP) played a small role in CH_4 emission (relative importance of 0.1 and 0.3, respectively). SO_4^{2-} was not shown to control CH_4 emission.

4.4 Discussion

This chapter sought to describe *in situ* C exchange from two floodplain fens of differing nutrient status and the controlling factors on C dynamics, using the following research questions and hypotheses:

R.Q.2. How do CO_2 and CH_4 fluxes from Sutton and Strumpshaw Fen compare to European floodplain fens?

R.Q.3. What are the controlling factors on CO_2 and CH_4 exchange from floodplain fens?

H_4: R_{eco} will be controlled by peat temperature, VGA, water level and porewater NO_3^- and PO_4^{3-} concentration.

H_5: GPP will be controlled by air temperature, PAR, VGA, water level and porewater NO_3^- and PO_4^{3-} concentration.

H_6: CH_4 emission will be controlled by peat temperature, VGA, water level, redox conditions, barometric pressure, and porewater NO_3^- and PO_4^{3-} concentration.

Relatively few studies have quantified C exchange from temperate floodplain fens. Currently only one other *in situ* study has been undertaken in the UK: Morrison et al. (2013) investigated CO_2 exchange at an intensively cultivated lowland peatland, with very little peat remaining. However, there has not previously been a study that investigates C exchange from peat and ditch networks at floodplain fen sites under conservation management in the UK. With a global push to restore peatlands to become C sinks as a climate change mitigation scheme (O'Sullivan and Emmer, 2011, Moxey and Moran, 2014), it is necessary to understand C dynamics in peatlands under conservation management.

4.4.1 Observed fen C exchange in sites of differing nutrient status

4.4.1.1 Observed fen CO_2 exchange

Differences in observed R_{eco} and NEE are reported for the 16 month sampling period (R.Q.2); due to intermittent sampling over the 16 month sampling period, seasonality is difficult to argue. However, sampling over a 16 month period did allow the quantification of CO_2 exchange over two growing seasons and two successive year's peak biomass,

when greatest GPP occurs. This proved to be useful in the interpretation of flood events (Figure 43) on plant dynamics (Figure 44) and subsequently, C exchange.

Greatest rates of R_{eco} and GPP were observed during the summer months due to warmer temperature (Figure 31), higher incoming solar radiation (PPFD; Figure 48) and phenology of the plants (Figure 44). Temperature was shown in this study to be an important controlling factors on R_{eco} and GPP (Table 33). This corroborates with other studies, where temperature was a significant controlling factor on CO_2 exchange as it alters primary and secondary plant metabolism (Berry and Bjorkman, 1980), as well as heterotrophic respiration and gas release (section 2.3.3.1) (Audet et al., 2013a, Kandel et al., 2013b, Koebsch et al., 2013a). Longer days and greater incoming solar radiation within summer months result in greater photosynthetic uptake of CO_2, along with greater green photosynthesising area (Laine et al., 2007a, Riutta et al., 2007b). R_{eco} and NEE were less in autumn and spring months due to cooler temperature and the senescence/growth of vegetation (section 4.3.2). Winter fluxes were only quantified at Sutton Fen in January 2013, when the site was a net emitter of CO_2 due to the lack of aboveground green vegetation to photosynthesise (Figure 44). VGA was shown to be an important controlling factor on GPP (Table 33). The occurrence of aboveground green biomass is essential in GPP and plant metabolism. Huth et al. (2012) also observed net winter time emissions due to a lack of aboveground green biomass to sequester CO_2.

Observed CO_2 exchange was greater in spring and summer months of 2012 than in 2013 for both R_{eco} and NEE due to a larger VGA (Figure 44). It is possible that the greater VGA in 2012 than in 2013 produced higher labile root exudates for heterotrophic respiration (Badri and Vivanco, 2009). The importance of VGA on R_{eco} (Table 33) suggests that the priming effect may occur in these environments. However, as this was not directly measured in this study, alterations in R_{eco} cannot be definitively attributed to the priming effect or root exudates. The flooding of Sutton and Strumpshaw Fen during January and March 2013 (Figure 43) may have put extra stress on vegetation at the beginning of the growing season and prevented plant growth (section 3.3.7). Wilson et al. (2007b) also observed differences between two sampling years, with greater *P. arundinacea* and *T. latifolia* VGA in 2003 than in 2002 due to less rainfall (annual rainfall was 24 % higher and 4 % lower in 2002 and 2003, respectively, from the long term average) and lower water levels, translating into greater NEE and R_{eco} (Wilson et al., 2007b). Differences in NEE and R_{eco} in Wilson et al. (2007b) between the two years vary

but maximum NEE and R_{eco} in 2003 were approximately 1000 mg CO_2 m^{-2} h^{-1} greater than in 2002.

Water level was also an important controlling factor on R_{eco} and GPP (Table 33). In January 2013 and March 2013, flood events significantly increased the water level at Sutton Fen (Figure 32; *in situ* CO_2 exchange was not measured at Strumpshaw Fen during this period). These events had an impact on R_{eco} and GPP in both the short- and long-term. In the short-term, R_{eco} increased 136 % (based on average hourly fluxes for all collars) from November 2012 to January 2013 at Sutton Fen (Figure 41A). A decrease in R_{eco} would normally be expected in January due to a decrease in air temperature (Figure 31) as observed in Wilson et al. (2007b). However, the high water levels at Sutton Fen acted as a thermal buffer and insulated against the low air temperature (Figure 53), increasing surface peat temperature to approximately 5 °C and possibly facilitating anaerobic decomposition of organic matter, as observed in Wilson et al. (2007b). The March 2013 flood event had the opposite effect on R_{eco}, decreasing fluxes by 72 % (based on average hourly fluxes for all collars) from January 2013 to March 2013 (Figure 41A), less than fluxes in November 2012. A drop in R_{eco} due to flooding has been shown in a number of other studies (Waddington et al., 2010, Hatala et al., 2012, Koebsch et al., 2013a) and is attributed to anaerobic conditions that ensue post flooding.

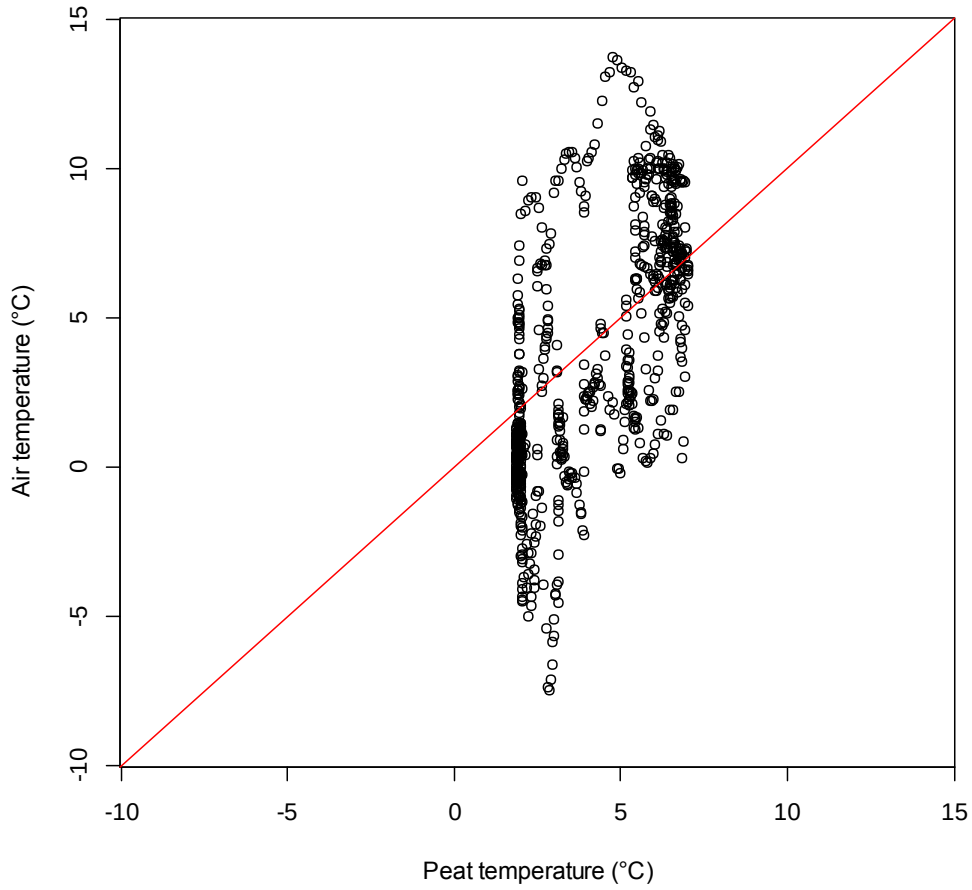


Figure 53 Surface peat temperature versus air temperature at Sutton Fen in January 2013.

The flood water chemistry may also help explain the differences between CO_2 exchange between January and March 2013. SRP and NO_3^- were found to be controlling factors on R_{eco} and GPP (Table 33). However, no significant difference was observed in porewater NO_3^-, SRP or SO_4^{2-} concentrations between January and March 2013 at Sutton Fen. The lack of difference may be due to the depth at which porewater samples were taken at (30 cm below peat surface) and the height of the water column above the peat surface during the two flood periods (between 20 to 30 cm above the peat surface). Potentially the macronutrients may not have diffused down to the porewater sampling depth due to mineralisation processes within the water column and the uptake of nutrients by plants and microbes at the peat surface. The chemistry of the water column above the peat was not measured, but ditch water chemistry should provide information on the floodwater chemistry. Converse to porewater, ditch water NO_3^-, SO_4^{2-} and Cl^- concentrations at Sutton Fen were significantly greater in March 2013 than in January 2013 ($t_{17.181} = -63.8637$, $p < 0.001$, $t_{14.196} = -35.7138$, $p < 0.001$ and $t_{14.267} = -18.4075$, $p < 0.001$ for NO_3^-, SO_4^{2-} and Cl^-, respectively). Salinity has been shown in a number of studies to negatively affect both vegetation and microbial processes (Baldwin and

Mendelssohn, 1998, Drake et al., 2002, Morrissey et al., 2014). Under anoxic conditions, SO_4^{2-} is reduced to H_2S, a phytotoxin, within peatlands and has been shown to adversely affect growth of wetland vegetation (Baldwin and Mendelssohn, 1998). Additionally, the effects of salinity has been shown to inhibit metabolic functioning by reducing protein synthesis, and in turn reducing C sequestration and OM accumulation, and cause cellular osmotic stress (Koch et al., 1990, Baldwin and Mendelssohn, 1998, Morrissey et al., 2014). Vile et al. (2003) also observed an initial reduction in potential CO_2 production with SO_4^{2-} in an *ex situ* microcosm experiment due to salinity intolerance of the microbial population. The greater ditch water SO_4^{2-} concentrations at Sutton Fen in March 2013 than in January 2013 may have resulted in the decrease in R_{eco} observed (Figure 41).

Over a longer timescale, the two flood events at the beginning of 2013 (Figure 43) significantly altered plant dynamics within the two sites. Peak biomass (September) VGA decreased significantly at Sutton between 2012 and 2013 ($t_{10} = 2.267$, $p = 0.047$). This decrease was especially pronounced at Sutton fen due to the greater abundance of sedges (*Carex spp.*, Figure 46B and *C. mariscus*, Figure 45A) and a lesser abundance of *P. australis* (Fig 46A). Sedges have an earlier growing season (Grime et al., 2007) than *P. australis* (Grunfeld and Brix, 1999, Engloner, 2009), putting more stress on the sedge communities as water levels declined by the time reeds started to grow from May onwards. The majority of dominant plant species at both sites have been shown to resist flooding (Brix, 1989, Visser et al., 2000, Grime et al., 2007). However, the amount of carbohydrates stored in a plant's rhizomes dictates the maximum water level that shoots can overgrow at the beginning of the next growing season (Blom, 1999, Koebsch et al., 2013a). If the water level is above this, greater amounts of stress is put on a plant and impacts on aboveground biomass. *Carex spp*. have been shown to be able to survive up to 40 days completely submerged (Moog, 1998). The increase in salinity along with the flood event in March 2013 (section 3.3.6) will have also had a negative effect on the vegetation at the two sites. Plants respond to increases in salinity differently. *P. australis* is a relative tolerant plant to salinity and is found across salinity gradients from freshwater sites to brackish and saline sites (Hellings and Gallagher, 1992, Lissner and Schierup, 1997). However, other graminoids, such as *Carex spp.*, *J. subnodulosus* and *C. mariscus*, are not as tolerant to saline intrusion as *P. australis* (Grime et al., 2007). The dominance of *P. australis* at Strumpshaw Fen may have resulted in the lack of difference in VGA between 2012 and 2013. The generally higher concentrations of SO_4^{2-} and Cl^- at Strumpshaw Fen may have resulted in more saline tolerant plant species at the site. Whereas the greater abundance of other graminoidal species, such as *Carex spp.*, *J.*

subnodulosus and *C. mariscus,* and the lesser dominance of *P. australis* at Sutton Fen may have resulted in the significant reduction in VGA between years.

The alterations to the vegetation by inundation at Sutton fen may have had an impact on R_{eco} and GPP over the 2013 growing season as observed in Koebsch et al. (2013a); fluxes were less than in 2012. R_{eco} and NEE in June 2013 was significantly less than in June 2012 for both Sutton (t_{10} = 2.346, p = 0.041 and $t_{3.324}$ = -3.301, p = 0.027, respectively) and Strumpshaw fen (t_7 = 2.917, p = 0.022 and t_5 = 1.561, p = 0.017). NEE remained significantly less in 2013 than in 2012 for July, August and September (t_6 = -3.878, p = 0.008, t_{10} = -4.944, p = 0.001 and t_9 = -5.818, p < 0.001, respectively) at Sutton Fen. Additionally, low CO_2 and O_2 diffusion rates in water and submergence of plant tissue may have physically constrained CO_2 exchange (Koebsch et al., 2013a). Plant aboveground biomass that had not grown above the water level in March and April 2013 may not have been included in VGA estimates due to difficulties in observing and measuring individual plants below the water surface. Although every best effort was made to include all vegetation in the VGA estimate, high water levels and the increase in sediment deposition from the river made it difficult to see and some underestimation may have occurred. This sediment deposition may have also reduced GPP during flooding periods as light cannot penetrate the boundary created by the sediment layer.

VGA was within the literature values for lowland fens (Figure 54) (Wilson et al., 2007a, Wilson et al., 2007b); however summer values for Strumpshaw Fen are higher than those reported in the literature. The nutrient status as this site may be a causal factor in these high values. High values are also observed in leaf area index (LAI) for other environments dominated by *P. australis* (Figure 54). LAI is a measure of total green leaf area, whilst VGA includes both green leaf and green stem area, resulting in larger VGAs than LAIs. Values reported in the literature for LAI (Figure 54) are greater than the maximum VGA value for Strumpshaw.

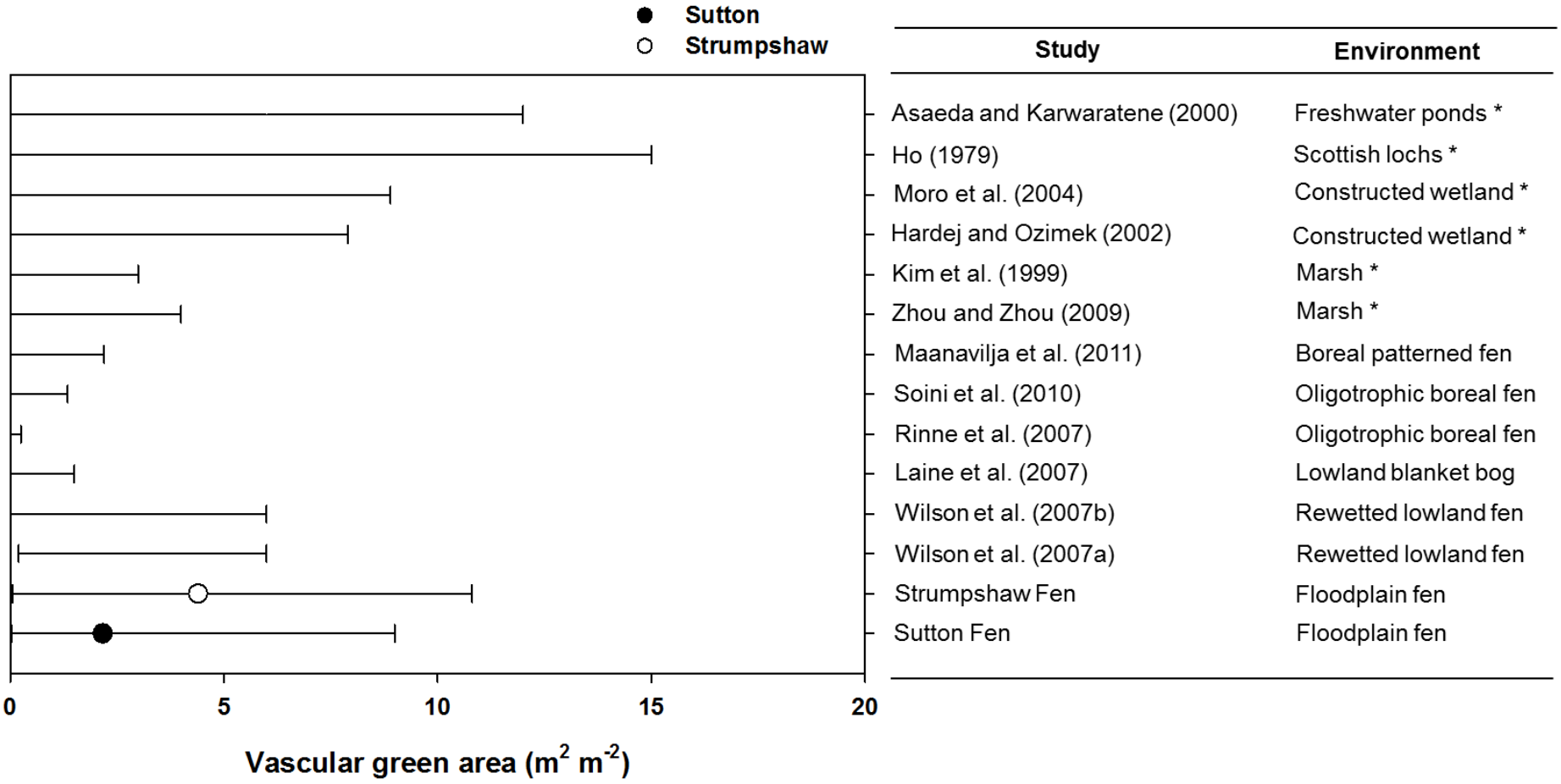


Figure 54 Comparison of VGA with ranges in literature values in differing environments and Sutton and Strumpshaw Fen (range plus mean indicated by circle). * indicates leaf area index (LAI) values used instead of VGA. Points represent mean values and bars denote minima and maxima values.

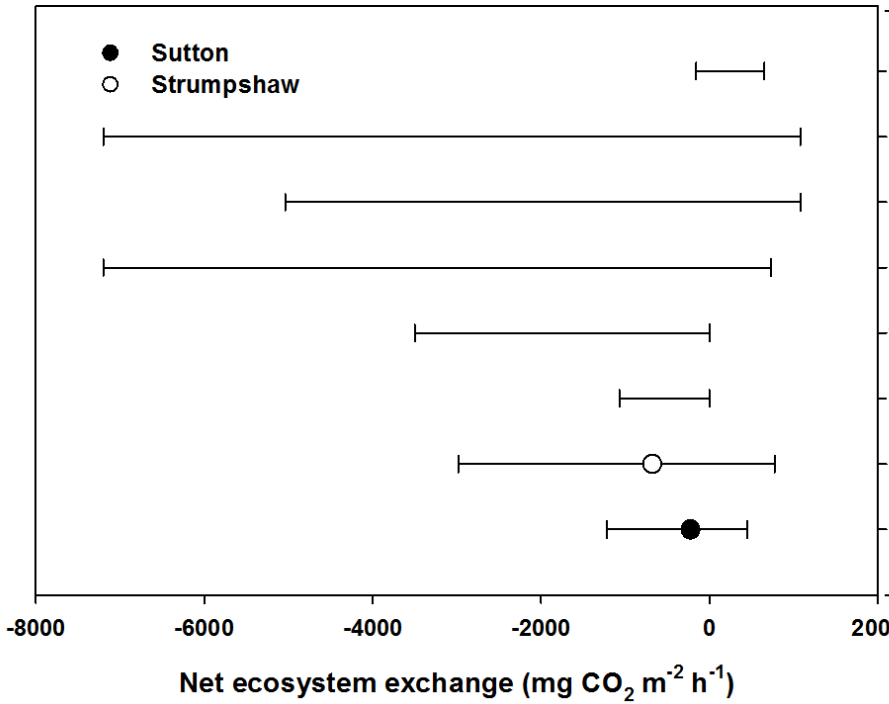
Water level had a large impact on R_{eco} (Table 33), albeit altering mechanisms differently to changes in GPP due to water level dynamics. For $R_{eco,}$ it is suspected that higher CO_2 emissions in August and September 2013 were potentially caused by a greater drop in water level in 2013 than 2012 (Figure 32; $t_{92} = 28$, $p < 0.001$ and $t_{80} = 25$, $p < 0.001$ for Sutton and Strumpshaw Fen, respectively). This greater drop in water level at both Sutton and Strumpshaw Fen will have had an impact on autotrophic and heterotrophic respiration. The greater oxic portion of the peat profile will have enabled aerobic heterotrophic decomposition to occur deeper within the peat profile and resulted in greater R_{eco} at both sites. The effects of water level draw down and water stress on autotrophic respiration are less clear. Generally as water levels decrease and water stress occurs, plants reduce their primary metabolic functioning and thus autotrophic respiration decreases (Ryan, 1991, Seigler, 1998, López-Gómez and Lluch, 2011). However, maintenance process (secondary metabolism) remain to try to cope with the stress and keep the plant alive (Seigler, 1998) by increasing belowground biomass in search of water, in turn causing an increase in autotrophic respiration. Autotrophic contributions to R_{eco} have been estimated via models to be between 10 and 50 % in peatlands (Lafleur et al., 2005), depending on the time of year and type of peatland. Relative contribution of autotrophic and heterotrophic respiration vary seasonally, depending on plant growth or senescence. As plants grow, more carbohydrates are metabolised to help increase above- and belowground biomass, as well as maintain primary metabolism. However, primary and secondary metabolic functioning reduces in deciduous plants with senescence. Koebsch et al. (2013a) also observed a significant increase in R_{eco} with a decrease in water level and attributed the increase in fluxes to heterotrophic respiration occurring within the greater oxic portion of the peat profile.

Considerable wintertime losses via R_{eco} were observed at Sutton Fen (Strumpshaw Fen not visited during the winter) in January 2013, which were attributed to the thermal buffering of the high water tables at the site (section 3.3.7; Figure 53). The extra water column above the peat surface (between 20 and 40 cm above the peat surface; Figure 32) insulated the peat from the cold air temperatures during the sampling period on January 2013 (Figure 31 and 53). January 2013 fluxes were greater than November 2013 and March 2013 for Sutton Fen (Figure 41), despite warmer air temperatures in the months pre- and succeeding January 2013. The decrease in water level in August and September 2013 also increased GPP in comparison with 2012. GPP has been shown to decrease in peatlands plant species with decreases in water level due to plants being put under water stress and subsequently stomata closing to reduce water vapour losses, impacting on photosynthetic uptake of C (Pagter et al., 2005). However, Saltmarsh et al.

(2006) showed an increase in photosynthetic uptake in *P. australis* under slightly drained to mild stress. Instead of reducing photosynthetic capacity to cope with drought stress, such as species like *C. mariscus*, *P. australis* alters leaf area via leaf mortality to adjust to water availability, maintaining high assimilation levels (Saltmarsh et al., 2006).

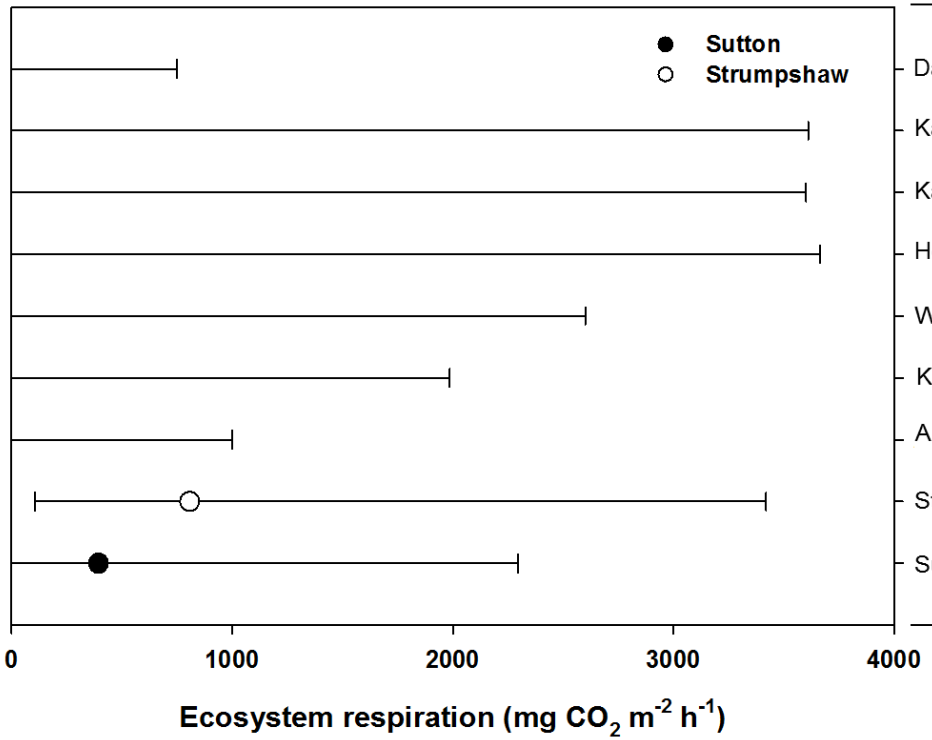
There are a small number of notable studies that have investigated CO_2 exchange within lowland fens in Europe (Figure 55 and Figure 56), including Wilson et al. (2007b; CO_2 dynamics at an Irish lowland fen), Huth et al. (2012; winter GHG exchange from a fen under conservation management; Neuenkirchener Niederung), and Audet et al. (2013a, 2013b; GHG exchange from Danish riparian fens; Odderbæk, Karup, Haderup and Simested). Wilson et al. (2007b) measured CO_2 exchange during 2002 and 2003 at a site containing *P. arundinacea*, *P. australis*, *T. latifolia, A. stolinifera, M. aquatica* and *G. palustris*, similar species to Sutton and Strumpshaw, to investigate rewetting on GHG fluxes. In Wilson et al. (2007b), both R_{eco} and NEE followed a seasonal patterns, with fluxes ranging from ~ 100 to 2600 and ~ 1000 to -3500 mg CO_2 m^{-2} h^{-1} (negative values equate to uptake of CO_2), respectively. A wider range in R_{eco} and NEE was observed in Wilson et al. (2007b) than at Sutton and Strumpshaw. The authors attributed the wide range in fluxes to the recent restoration of the site and the climatic conditions of the sampling period (Wilson et al., 2007b).

Despite measures to try to reduce the impact of air temperature and humidity changes on fluxes during chamber runs in the field, alterations to both were observed in the field. To help abate the issue of creating artificial microenvironments whilst sampling, temperature and pressure were corrected for during flux calculations (see section 4.2.6). However, humidity was not corrected for during calculations. CO_2 fluxes were calculated from IRGA data, which was only run at the beginning of a chamber being deployed for the first 5 minutes. During this period, negligible alterations to humidity occurred and thus it is anticipated that there was a minimal effect of humidity on CO_2 fluxes.



Study	Environment	Dominant plant species	Sampling period	Sampling frequency	Country
Huth et al. (2012)	Floodplain fen	*A. pratensis**	November 2009 – March 2010	Biweekly	DE
Kandel et al. (2013b)	Drained cultivated lowland fen	*P. arundinacea*	September 2010 – September 2011	Biweekly	DK
Kandel et al. (2013a)	Drained cultivated lowland fen	*P. arundinacea*	June 2011 – September 2011	Biweekly	DK
Hendriks et al. (2007)	Floodplain peat meadow	*P. arundinacea*	January 2004 – December 2006	10 Hz	NL
Wilson et al. (2007b)	Lowland fen	*P. australis*	April 2002 – December 2003	Biweekly	IRE
Koebsch et al. (2013)	Lowland fen	*P. australis*	May – October 2009 - 2011	10 Hz	DE
Strumpshaw Fen	Floodplain fen	*P. australis*	June 2012 – September 2013	Monthly	UK
Sutton Fen	Floodplain fen	*P. australis*	June 2012 – September 2013	Monthly	UK

Figure 55 Comparison of ranges in net ecosystem exchange in Danish (DK), German (DE), Dutch (NL) and Irish (IRE) fen sites within the literature and Sutton and Strumpshaw Fen. Points represent mean values and bars denote minima and maxima values. * *Alopecurus pratensis* L. (1753).



Study	Environment	Dominant plant species	Sampling period	Sampling frequency	Country
Danevčič et al. (2012)	Drained fen grassland	*A. elatius**	November 2009 – March 2010	Biweekly	SI
Kandel et al. (2013b)	Drained cultivated lowland fen	*P. arundinacea*	September 2010 – September 2011	Biweekly	DK
Kandel et al. (2013a)	Drained cultivated lowland fen	*P. arundinacea*	June 2011 – September 2011	Biweekly	DK
Hendriks et al. (2007)	Floodplain peat meadow	*P. arundinacea*	January 2004 – December 2006	10 Hz	NL
Wilson et al. (2007b)	Lowland fen	*P. australis*	April 2002 – December 2003	Biweekly	IRE
Koebsch et al. (2013)	Floodplain fen	*P. australis*	May – October 2009 - 2011	10 Hz	DE
Audet et al. (2013a)	Floodplain fen	*A. stolinifera*	May 2010 – December 2011	Triweekly	DK
Strumpshaw Fen	Floodplain fen	*P. australis*	June 2012 – September 2013	Monthly	UK
Sutton Fen	Floodplain fen	*P. australis*	June 2012 – September 2013	Monthly	UK

Figure 56 Comparison of ranges in ecosystem respiration in Danish (DK), German (DE), Dutch (NL), Irish (IRE) and Slovenian (SI) fen sites within the literature with Sutton and Strumpshaw Fen. Points represent mean values and error bars denote minima and maxima values. * *Arrhenatherum elatius* (L.) P. Beauv. ex J. Presl & C. Presl (1819).

4.4.1.2 Observed fen CH_4 fluxes

Fen CH_4 fluxes varied temporally and between Sutton and Strumpshaw Fens (Figure 51; R.Q.2). Fluxes altered over the sampling months, albeit less clear than for CO_2 exchange (Figure 41). However, this is due to CH_4 emissions not being directly controlled by photosynthesis as CO_2 is; although, fluxes were greater in the summer months due to warmer temperatures (Table 33), as observed in other studies (Schrier-Uijl et al., 2010b, Audet et al., 2013b, Minke et al., 2014). Peat temperature was found to be a significant controlling factor on CH_4 emissions at Sutton and Strumpshaw Fen (Table 33). In other studies, an increase in water level has been shown to increase CH_4 emissions (Kettunen et al., 1999). This was not observed at Sutton and Strumpshaw, as water level was found to be a lesser important controlling factor (Table 33), despite the water level being above the peat surface during the autumn and winter months (Figure 32). The reduced temperature during this period may play a role in the reduction in emission (R_{87} = 0.44, p < 0.001); although, it is hypothesised that the March flood event altered the C dynamics at both sites in two ways. Firstly, the inundation put stress on the vegetation at the beginning of the growing season, limiting plant growth (Figure 44) and thus potentially altering root exudate release of labile C for methanogenesis. Secondly, the flood events brought in a nutrient/saline pulse that inhibited/reduced methanogenesis at both sites as CH_4 fluxes were significantly less than in January 2013 and the early summer 2012 fluxes (Figure 50).

A reduction in CH_4 emission at Sutton Fen in March 2013 was observed (Figure 51) and is suspected to be caused by the flooding that occurred in January and March 2013 bringing in either a saline or nutrient pulse (Figure 26 and 28). Salinity, NO_3^- and SRP were shown to be controlling factors on CH_4 emissions (Table 33). Pore- and ditch water SO_4^{2-} concentrations at Sutton Fen were significantly greater in March than in January 2013 ($t_{5.148}$ = 19.892, p = 0.0101 and $t_{14.196}$ = -35.7138, p < 0.001 for pore- and ditch water, respectively). NO_3^- concentrations were significantly greater in ditches at Sutton Fen in March 2013 than in January 2013 ($t_{17.181}$ = -63.8637, p < 0.001). Both SO_4^{2-} and NO_3^- have been shown to act as an electron acceptor in anaerobic CH_4 oxidation (AOM) within peatlands, as well as acting as methanogenic inhibitors (section 2.3.4.3) (Smemo and Yavitt, 2011, Blazewicz et al., 2012, Gupta et al., 2013).

Temperature greatly alters CH_4 emission (Table 33). However, it is not thought to be causing the spatial variability observed at the two sites as peat temperatures between

collars do not vary significantly between the two sites (Figure 57). Plants have been shown to produce more root exudates when under nutrient-poorer conditions as a mechanism to release P through a symbiotic relationship between plants and fungal/microbial communities in the rhizosphere (Koelbener et al., 2010). This process may have a small effect at the two sites; however, it is not thought to be a main driving factor on differences in CH_4 emissions between the two sites as this priming effect is not observed in R_{eco} at Sutton Fen, where fluxes are less than at Strumpshaw Fen (section 4.3.1). Instead, it is thought that substrate quality and nutrient availability may be more of an influencing factor (Table 33). Significantly greater porewater NO_3^- and SO_4^{2-} concentrations (Figure 26 and Table 16) at Strumpshaw Fen result in more oxidised conditions at the site (shown as Fe^{2+} data) in comparison to the more reduced conditions at Sutton Fen, which promotes methanogenesis. Additionally, the significantly greater porewater NO_3^- and SO_4^{2-} concentrations (Figure 26 and Table 16) at Strumpshaw Fen may inhibit methanogenesis at the site (section 2.3.4.2), as well as potentially promoting AOM using the two macronutrients (section 2.3.4.3).

In 2013 the pattern in CH_4 emission changes, with no site clearly emitting more CH_4 than the other. This alteration in pattern may be due to the alteration in VGA (Figure 44) caused by the flood event in March 2013 (see section 4.4.1.1 for effects of flooding on VGA). VGA was shown to be a controlling factor on CH_4 emission, despite having a low relative importance (Table 33). The larger range in fluxes at Strumpshaw is thought to be due to two high emission events occurring in August 2012 and July 2013 (Figure 51), attributed to steady ebullition (section 2.3.2). It is thought that these high emissions in August 2012 and July 2013 are caused by steady ebullition as the two fluxes are an order of magnitude greater in both months than other collars at Strumpshaw sampled within a couple of days of each other. Peat structure (section 3.3.1) is thought to potentially be the cause for the occurrence of steady ebullition events at Strumpshaw Fen and not at Sutton Fen. CH_4 bubbles accumulate within the peat until a trigger induces the transport of the bubbles through a preferential route. In the case of Strumpshaw Fen, the dense root mat 50 cm below the surface inhibits the movement of CH_4 bubbles from deeper within the peat until the preferential pathway is found. The large amount of dead *P. australis* culms at Strumpshaw Fen could act as conduits for steady ebullition, bypassing the dense root mat.

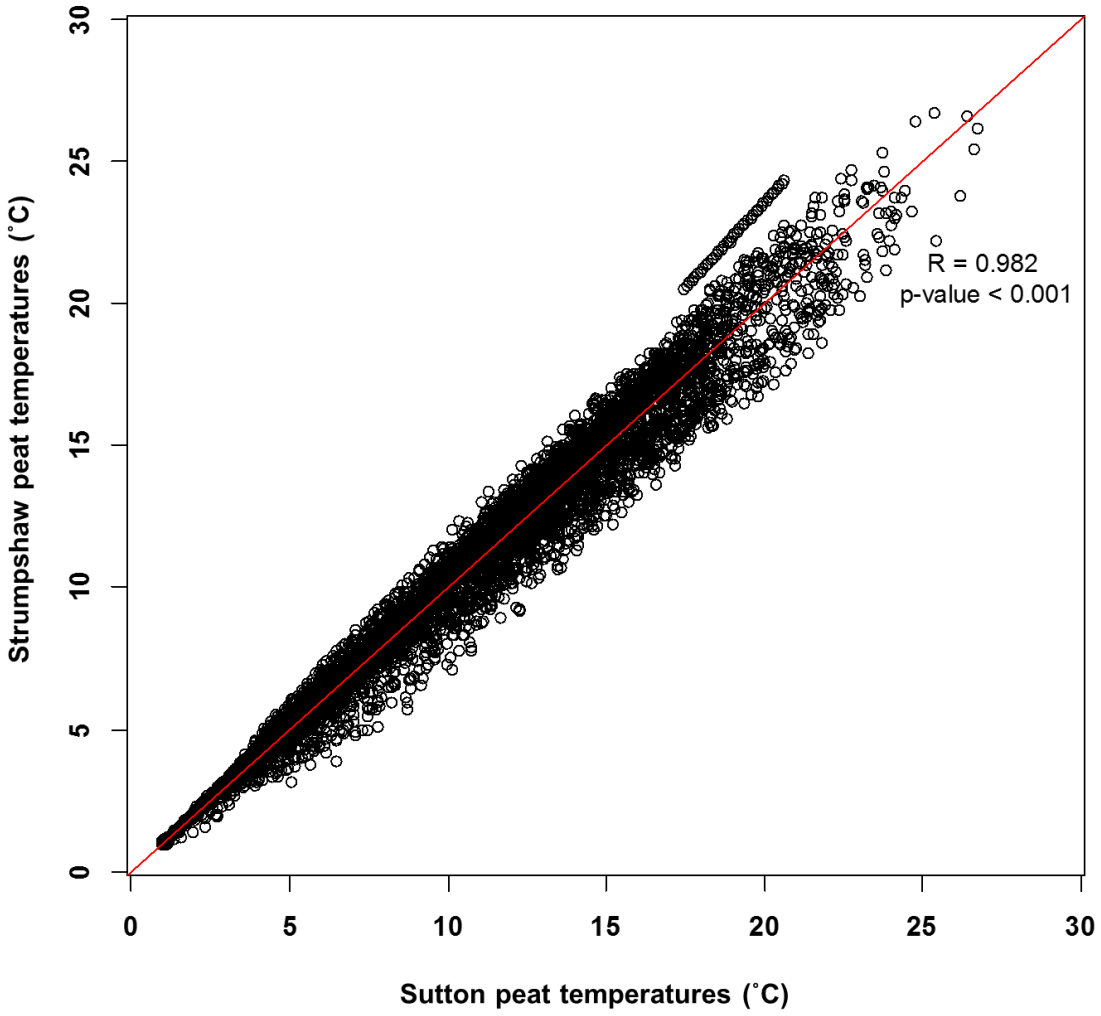
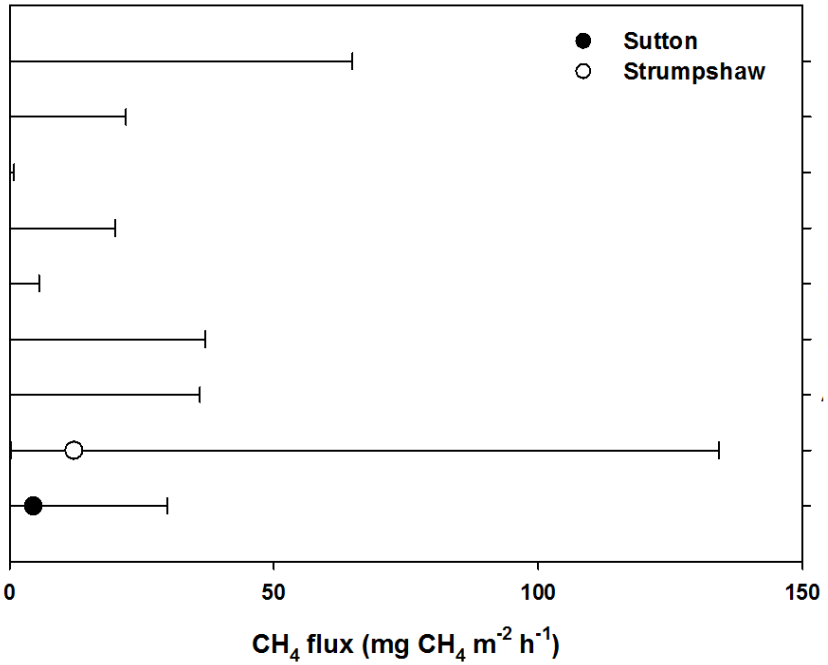


Figure 57 Comparison of surface peat temperature (tiny tag data, 5 cm below peat surface) for Sutton and Strumpshaw fen. Red line shows 1:1 line.

There are a small number of notable studies that have investigated CH_4 fluxes within floodplain fens in Europe (Figure 58), including Huth et al. (2012; winter GHG exchange from a fen under conservation management; Neuenkirchener Niederung), and Audet et al. (2013a, 2013b; GHG exchange from Danish riparian fens; Odderbæk, Karup, Haderup and Simested). CH_4 emission from the Danish sites followed seasonal patterns, with greater emission in the summer and smaller in the winter. Danish CH_4 fluxes ranged from 0 to 37 mg CH_4 m^{-2} h^{-1} (Audet et al., 2013a, Audet et al., 2013b), similar to fluxes at Sutton and Strumpshaw Fens. Only two fluxes were not within the Danish range, 134 and 105 mg CH_4 m^{-2} h^{-1} for August 2012 and July 2013, respectively, at collar 5 at Strumpshaw Fen. It is assumed that these two fluxes were caused by steady ebullition, as other summer fluxes from this collar were at least one order of magnitude smaller (Figure 50). January 2013 CH_4 emissions were greater at Sutton Fen than winter

emissions in Neuenkirchener Niederung in the north of Germany, where the maximum flux was 0.49 mg CH_4 m^{-2} h^{-1} (Huth et al., 2012). The smallest flux from Sutton Fen during January 2013 was significantly larger (1.2 mg CH_4 m^{-2} h^{-1}), which is more in the range of Karup and Haderup winter fluxes (Audet et al., 2013b). Huth et al. (2012) attributed the small winter fluxes to the weather conditions, as the winter of 2009/2010 was the harshest for 30 years in Mecklenburg-Western Pomerania.

Schrier-Uijl et al. (2010b) found that electrical conductivity was significantly negatively correlated with CH_4 emission. However, fluxes from this study are significantly less than at Strumpshaw Fen (higher electrical conductivity between sites in this study; section 3.3.6). The difference in emission could possibly be due to the cutting of the vegetation at the Dutch sites between 3 and 4 times over the growing season (Schrier-Uijl et al., 2010b). Cutting vegetation reduces root exudate release into the peat substrate as carbohydrates produced via primary metabolism are focused on above-ground biomass growth (secondary metabolism) to increase photosynthetic inputs (Badri and Vivanco, 2009). No direct measurement of peat quality or nutrient status were made in the Schrier-Uijl et al. (2010b) study; however, surface peats (top 25 cm) were clayey-peat mixtures on top of 12 m of peat. The surface peats at the two Dutch sites contain less OM and potentially poorer quality peat. Lesser CH_4 emissions were also observed in Hendriks et al. (2007) than Strumpshaw Fen, despite the electrical conductivity being lower at Strumpshaw Fen and the vegetation was very similar as to that in this study. Hendriks et al. (2007) also cut the vegetation to size to fit into the chambers that were used at Horstermeer, which is thought to influence the difference in CH_4 emission between studies. Difference in peat quality between Horstermeer and Strumpshaw Fen may also be explained by the difference in CH_4 emissions between sites, with substrate at Horstermeer primarily composed of clayey-peat mixtures throughout the peat profile (Hendriks et al., 2007).



Study	Environment	Dominant plant species	Sampling period	Sampling frequency	Country
Hendriks et al. (2010a)	Floodplain peat meadow	*P. australis*	November 2009 – March 2010	Biweekly	NL
Schrier-Ujil et al. (2010a)	Floodplain fen	*Carex spp.*	January 2005 – November 2008	Monthly	NL
Huth et al. (2012)	Floodplain fen	*A. pratensis**	November 2009 – March 2010	Biweekly	DE
Huth et al. (2013)	Floodplain fen	*P. australis*	July 2011 – June 2012	Biweekly	DE
Augustin et al. (1998)	Floodplain fen	*C. mariscus*	January – December 2012	Triweekly	DE
Audet et al. (2013b)	Floodplain fen	*Carex spp.*	June 2010 – July 2011	Triweekly	DK
Audet et al. (2013a)	Floodplain fen	*A. stolinifera*	May 2010 – December 2011	Triweekly	DK
Strumpshaw Fen	Floodplain fen	*P. australis*	June 2012 – September 2013	Monthly	UK
Sutton Fen	Floodplain fen	*P. australis*	June 2012 – September 2013	Monthly	UK

Figure 58 Comparison of literature ranges in CH_4 fluxes from Danish (DK), German (DE) and Dutch (NL) lowland fens and Sutton and Strumpshaw Fen. Points represent mean values and error bars denote minima and maxima values. * *Alopecurus pratensis* L. (1753).

The range of fluxes in Billett et al. (2015) were similar to Sutton Fen. Vegetation in the former study was similar to that at Sutton, with the German site being dominated by *P. australis, C. acutiformis* and *Typha latifolia*. Vegetation was not cut to size in this study, as in Hendriks et al. (2007) and Schrier-Uijl et al. (2010b), and the mean electrical conductivity (583 µS cm^{-1}) was similar to that at Sutton Fen (Billett et al., 2015). However, fluxes were slightly lower in Billett et al. (2015), possibly caused by the extremely wet summer during the sampling period.

4.4.2 Observed ditch C evasion

4.4.2.1 Ditch CO_2 fluxes

Even fewer studies have quantified ditch CO_2 evasion than fen CO_2 exchange in lowland fens. The majority of literature currently available is based on research undertaken in The Netherlands (Schrier-Uijl et al., 2010a, Vermaat et al., 2011). Findings from Sutton and Strumpshaw Fen showed evasion rates to be a significant source throughout the 16 month sampling period, despite evasion rates being significantly less than fen R_{eco} (*cf.* Figure 41 and Figure 50). In general, evasive CO_2 fluxes were an order of magnitude less than fen R_{eco}. Evasive fluxes from ditches are usually less than those observed from fenland due to a number of factors: the anaerobic conditions that prevail within the ditch and in the peat substrate at the bottom of the ditch promote anaerobic respiration and fermentation, which are less efficient processes than aerobic respiration (Moore and Dalva, 1993, Aerts and Ludwig, 1997, Blodau and Moore, 2003, Glatzel et al., 2004); supersaturation of the aquatic column occurs at a slower rate than molecular diffusion and is dependent on temperature, pressure and salinity (Weiss, 1974, Billett and Moore, 2008, Schrier-Uijl et al., 2010a); water has a different thermal capacity to peat and surface temperatures are generally less at higher temperatures (> 15 ºC; Figure 59) (Giauque and Stout, 1936, Waddington and Price, 2000); and the lack of macrophytes to oxidise the peat at the bottom of the ditch via plant-mediated transport (Blom, 1999). Despite the lesser fluxes, ditches are still important sources of CO_2 to the atmosphere as generally little CO_2 sequestration occurs, unlike during spring to autumn months in the fen where CO_2 is taken up via photosynthesis during daylight hours.

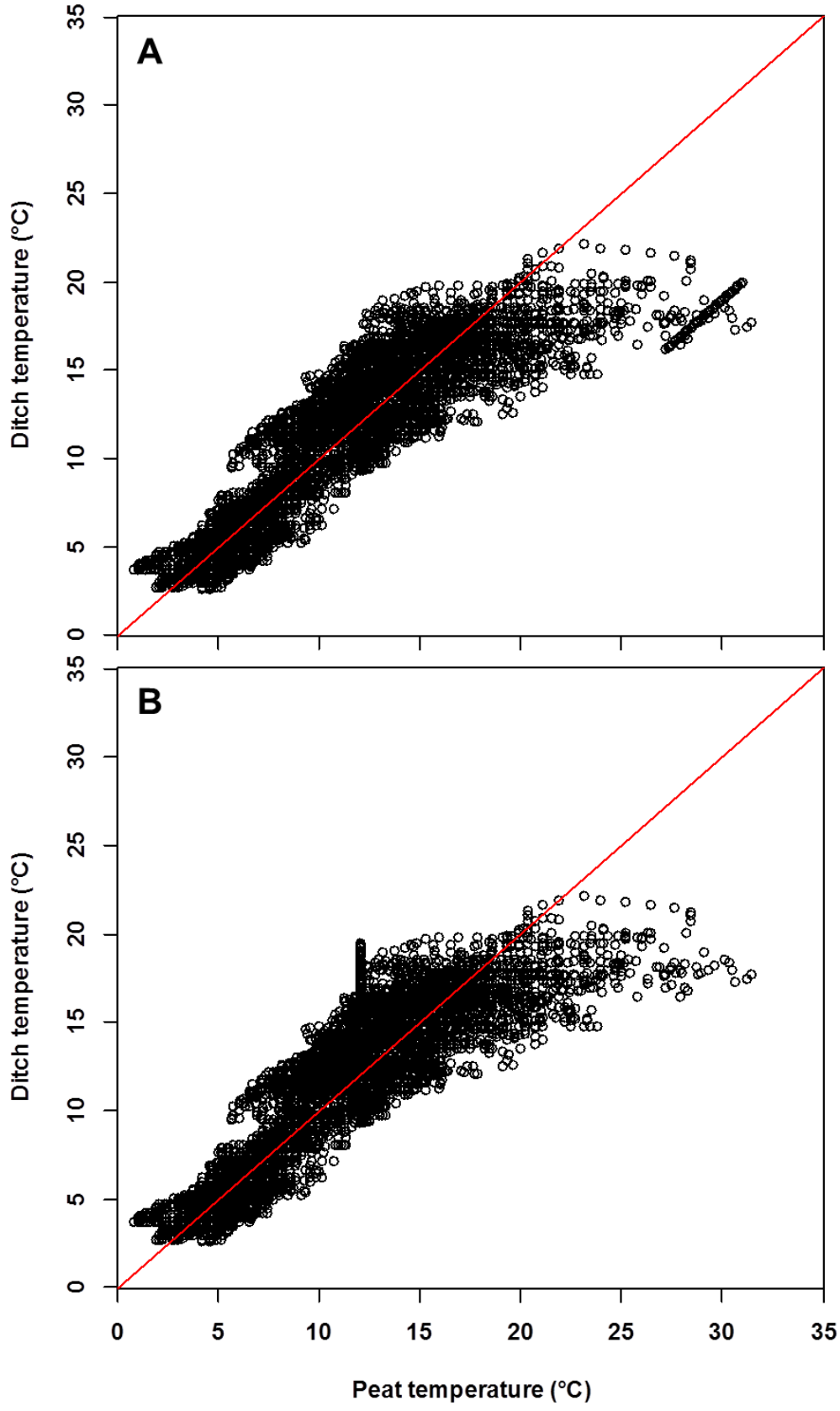
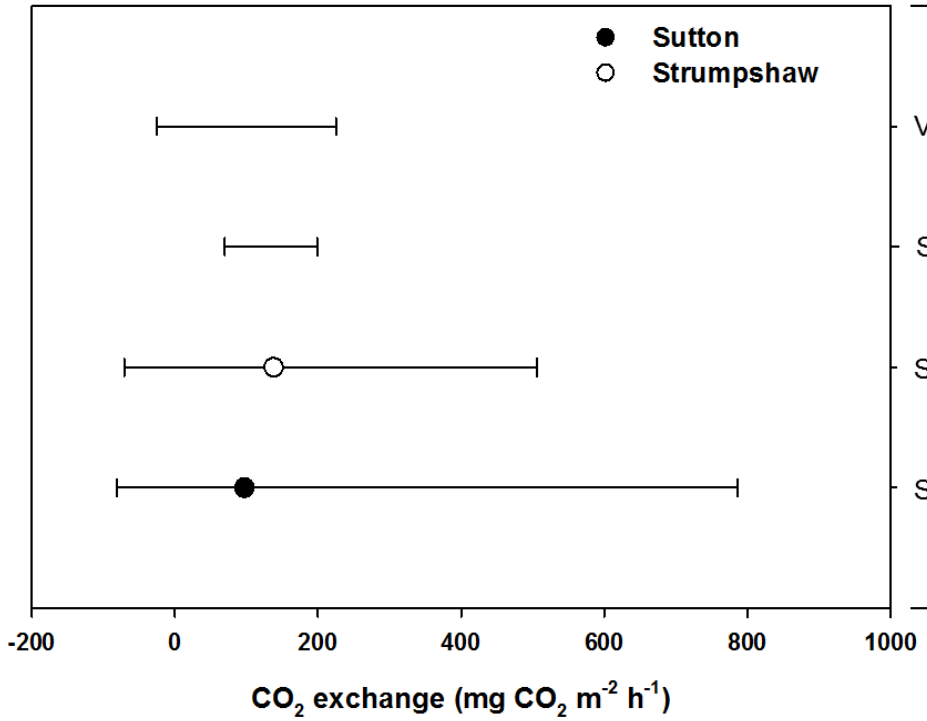


Figure 59 Hourly fen (average between collars) versus hourly ditch (average between ditches) temperatures at 5 cm below surface for (A) Sutton and (B) Strumpshaw Fen.

Previous studies have also shown ditches to be significant sources of CO_2 to the atmosphere. Ditch fluxes at Sutton and Strumpshaw were generally within the values reported in Vermaat et al. (2011) and Schrier-Uijl et al. (2010a) (Figure 60). Ditches in both Vermaat et al. (2011) and Schrier-Uijl et al. (2010a) were sources of CO_2 throughout the study period, as at Sutton and Strumpshaw (Figure 48). CO_2 evasion ranged from 69.6 to 199 mg CO_2 m^{-2} h^{-1} in Schrier-Uijl et al. (2010a) and 120 to 150 mg CO_2 m^{-2} h^{-1} in in ditches that intersect reed and sedge beds in Vermaat et al. (2011). In the latter study, It was assumed that the mean annual flux was lower (86 ± 21 mg CO_2 m^{-2} h^{-1} as opposed to 129 ± 8.2 mg CO_2 m^{-2} h^{-1} in Schrier-Uijl et al., 2010) due to summer fluxes not being sampled, as well as due to shading from vegetation surrounding the ditches. The effect of shading on CO_2 evasion was not investigated at Sutton and Strumpshaw Fen.

No uptake of CO_2 was observed in Vermaat et al. (2011) and Schrier-Uijl et al. (2010a). In April, June and July 2013, a small amount of uptake was observed at both Sutton and Strumpshaw Fen (Figure 50). It is assumed that some phytoplankton and benthic algae would have been able to sequester CO_2 from within the aquatic column, reducing evasive CO_2 fluxes to the atmosphere. Furthermore, the cool atmospheric conditions (Figure 31) during this period may have reduced respiration rates (Figure 50). CO_2 evasion in August and September 2013 at Sutton and Strumpshaw Fen were, however, much higher than reported in Vermaat et al. (2011) and Schrier-Uijl et al. (2010a). Fluxes at the sites in this study were much greater during August and September 2013 due to the lower water level than the previous year (Figure 32), allowing aerobic respiration to play a greater role in CO_2 production and altering transport processes from evasion to diffusion. As there is no aquatic column above the peat, CO_2 can be diffused directly to the atmosphere without having to first supersaturate a water body. No direct quantitative measurement of water level was taken in the ditches; however, the ditches were not very deep (c. 20 to 25 cm below the peat surface where evasion rates were measured) and observations taken at the time of sampling in August and September 2013 noted the water level below the peat at the bottom of the ditch. The increase in CO_2 emissions from ditches in August and September 2013 cause the large standard error observed in Table 28. Such a decrease in water level was not observed in Vermaat et al. (2011) and Schrier-Uijl et al. (2010a) and may explain the differences between August and September 2013 fluxes and the two studies.



Study	Environment	Sampling period	Sampling frequency	Country
Vermaat et al. (2011)	Floodplain fen	May 2008 – April 2009	Bimonthly	NL
Schrier-Ujil et al. (2010a)	Floodplain fen	January 2005 – November 2008	Monthly	NL
Strumpshaw Fen	Floodplain fen	June 2012 – September 2013	Monthly	UK
Sutton Fen	Floodplain fen	June 2012 – September 2013	Monthly	UK

Figure 60 Comparison of ranges in CO_2 evasion from floodplain fen ditches. Positive fluxes indicate net emission of CO_2. Points represent mean values and error bars denote minima and maxima values.

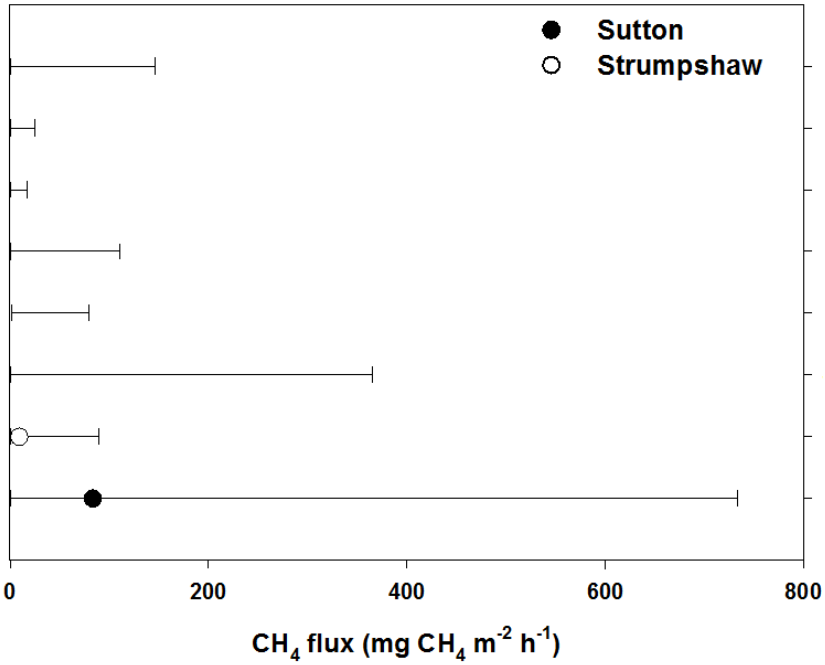
In comparison with other peatland environments where CO_2 evasion has been quantified, August and September 2013 fluxes are within the range found in the literature. Hamilton et al. (1994) and Roulet et al. (1997) measured CO_2 evasion from ponds within lowland peatlands within Canada. Hamilton et al. (1994) found evasive fluxes to range between 154 and 2375 mg CH_2 m^{-2} h^{-1} in two fen ponds ranging in depth between 0.1 and 0.75 m. Additionally, Hamilton et al. (1994) observed highest CO_2 evasion in September of the measurement period. Fluxes from fen ponds would be expected to be slightly greater than ditches as there would be greater disturbance at the surface water-atmosphere boundary layer due to wind as it is not as well protected byt the surrounding vegetation. Roulet et al. (1997) measured evasive fluxes from beaver ponds in a boreal peatland complex, observing fluxes ranging between -1793 to 4086 mg CO_2 m^{-2} h^{-1} (negative indicates net uptake of CO_2). Billett and Moore (2008) measured CO_2 fluxes in the Canadian Mer Bleu peatland complex, with fluxes ranging from 0 to 1820 mg CO_2 m^{-2} h^{-1}. Billett and Moore (2008) quantified fluxes in open and flowing surface water bodies, concluding that fluxes from the latter were 1.5 time greater. The authors attributed this to the water turbulence in flowing water disturbing the atmosphere-surface water boundary and inducing evasion (Billett and Moore, 2008). This is also corroborated with in Hope et al. (2001) and Billett and Harvey (2013), where CO_2 evasion ranged from 0 to c. 7000 mg CO_2 m^{-2} h^{-1}.

4.4.2.2 Ditch CH_4 fluxes

As for CO_2 evasion, relatively few studies have quantified ditch CH_4 evasion in lowland fens in comparison with fen CH_4 emissions. Currently six studies on CH_4 evasion in lowland fens are published (Figure 61) and the majority of the literature available is based on research undertaken in The Netherlands in agricultural sites (Hendriks et al., 2007, Schrier-Uijl et al., 2010a, Schrier-Uijl et al., 2010b, Vermaat et al., 2011). Ditch fluxes at Sutton and Strumpshaw Fen were positive throughout the 16 month sampling period and a significant source of CH_4 to the atmosphere. Previous studies have also shown ditches to be significant sources of CH_4, often greater than in the fens that they intersect (Hendriks et al., 2007, Schrier-Uijl et al., 2010a, Schrier-Uijl et al., 2010b, Vermaat et al., 2011). Generally, CH_4 evasion from ditches at Sutton and Strumpshaw Fen were an order of magnitude greater than fen emissions based on observed data (cf. Figure 51 and 52). Schrier-Uijl et al. (2010b) found that ditches emitted ~ 60 to 70 % of the total terrestrial CH_4 emitted from Stein and Oukoop peatland complexes studied. The extensively managed site in this study, Stein, had an average summer flux of 5 mg CH_4 m^{-2} h^{-1} (Schrier-Uijl et al., 2010b), which is significantly smaller than Sutton and Strumpshaw (109 ± 37 and 61 ± 12 mg CH_4 m^{-2} h^{-1}, and 24 ± 13 and 7.9 ± 3.8 mg CH_4

m^{-2} h^{-1} for 2012 and 2013 at Sutton and Strumpshaw, respectively). The highest flux observed at Oukoop by Schrier-Uijl et al. (2010b) of 366 mg CH_4 m^{-2} h^{-1} is significantly less than the highest flux in this study (734 mg CH_4 m^{-2} h^{-1} at Sutton Fen in September 2013). These two sites in Schrier-Uijl et al. (2010b) are, however, managed agricultural sites, which may account for smaller fluxes than observed at Sutton and Strumpshaw Fen, as NO_3^- and NH_4^+ have been shown to inhibit methanogenesis (section 2.3.4).

A sudden increase in CH_4 flux from Sutton Fen in September 2013 was observed (Figure 51) and is thought to be caused by the decrease in water level to below the ditch bottom at the site (Figure 43). As for the CO_2 evasion (section 4.3.3), this drop in water level below the ditch bottom altered the transport mechanism from evasion to diffusion and ebullition. As there is an absence of a water column to supersaturate above the peat, CH_4 that is emitted can diffuse from the peat into the atmosphere. Ditches are highly CH_4 productive environments due to the constant anoxic conditions caused by the aquatic column, as well as the lack of vegetation oxidising the peat substrate (Schrier-Uijl et al., 2010a). Additionally, Schrier-Uijl et al. (2010a) suggested that ditches are highly productive due to the nutrient inputs from fluvial inputs, resulting in greater reactants for methanogenesis to occur. It is possible that the change in transport mechanism observed in the ditches in August and September 2013 may cause the differences between fluxes in this study and Schrier-Uijl et al. (2010b). Additionally, the reduction of pressure from the absence of a water column above the peat in the ditch can induce ebullition. This demonstrates the importance of water level in ditches in regulating CH_4 emission by altering transport routes.



Study	Environment	Sampling period	Sampling frequency
Minkinnien and Laine (2006)	Minerotrophic fen[b]	January 1996 – December 1997	Biweekly
Hendriks et al. (2007)	Floodplain peat meadow[a]	January 2004 – December 2006	Monthly
Van den Pol-Van Dasselaar et al. (1999)	Floodplain fen[a]	January 1994 – October 1996	Monthly
Vermaat et al. (2011)	Floodplain fen[a]	May 2008 – April 2009	Bimonthly
Schrier-Ujil et al. (2010b)	Floodplain fen[a]	January 2005 – November 2008	Monthly
Schrier-Ujil et al. (2010a)	Floodplain fen[a]	January 2005 – November 2008	Monthly
Strumpshaw Fen	Floodplain fen	June 2012 – September 2013	Monthly
Sutton Fen	Floodplain fen	June 2012 – September 2013	Monthly

Figure 61 Comparison of ranges in literature values for ditch CH_4 fluxes from The Netherlands (a), Finland (b) and Sutton and Strumpshaw Fen. Points represent mean values and bars denote minima and maxima values.

Vermaat et al. (2011) observed greater CH_4 fluxes from nutrient enriched ditches; reed and sedge ditches had an average of 7 ± 1 mg CH_4 m^{-2} h^{-1} and ditches nutrient enriched by dairy effluent had averages of 17 ± 6 and 18 ± 8 mg CH_4 m^{-2} h^{-1}. The relationship with CH_4 evasion and ditch water NO_3^- and PO_4^{3-} concentrations was not observed in this study, as CH_4 fluxes were greater from Sutton Fen (Figure 52), despite NO_3^- and PO_4^{3-} concentrations being significantly lower at Sutton (Table 18). SO_4^{2-} and Cl^- concentrations are thought to be the cause of differences in CH_4 evasion (section 3.3.6). SO_4^{2-} has been shown to reduce CH_4 emission as either an inhibitor of methanogenesis or an electron acceptor for anaerobic CH_4 oxidation (Dise and Verry, 2001, Gauci et al., 2004, Smemo and Yavitt, 2011). Cl^- has been shown to alter the solubility of CH_4 in water, with greater concentrations reducing solubility (Yamamoto et al., 1976). Concentrations of SO_4^{2-} and Cl^- were greater in ditch water at Strumpshaw Fen (Table 18) than at Sutton Fen (Section 3.3.6). These differences in ditch water chemistry may explain variation in ditch CH_4 evasion, although it is something that needs to be further investigated.

4.4.3 Controlling factors on C dynamics

Currently, no previous study has shown the relative importance of controlling factors on terrestrial C exchange in floodplain fens (R.Q.3), making results from this modelling novel. The majority of studies within the literature use regression analysis to quantify if an environmental variable has a significant relationship with the dependent variable. Quantifying the relative importance of each significant factor using Akaike weights allows the sorting of importance of each environmental factor on C exchange. As peatlands are very heterogeneous, variation between collars was encapsulated within the model through the inclusion of collar as a random effect, instead of modelling sites independently of each other. This also improved the model as it increased the number of observations for the model.

4.4.3.1 R_{eco} controlling factors

Peat temperature, SRP, NO_3^-, VGA and water level were hypothesised as being controlling factors on R_{eco}; therefore H_4 was accepted. Peat temperature has been extensively shown to control R_{eco}, as it regulates microbial activity (Huth et al., 2012, Kandel et al., 2013a, Kandel et al., 2013b). Water level too has been cited as an important factor on R_{eco}, as it influences the rate of oxygen diffusion through the peat profile (Riutta et al., 2007b, Audet et al., 2013a, Kandel et al., 2013a). This controls the amount of peat respiring aerobically and anaerobically, with the former process being more efficient. SRP has been shown to increase respiration by increasing microbial

biomass and reactants available for mineralisation processes in laboratory studies and *in situ* in mineral soils studies (Amador and Jones, 1993, Kranabetter et al., 2005). Porewater SRP concentrations were low at both sites (Figure 26), especially at Sutton Fen where the majority of observed concentrations were less than the limit of detection (LOD; concentrations inputted as half the value of LOD, i.e. 0.05 mg L^{-1} SRP). However, this highlights the importance of SRP as a controlling factor on R_{eco}, with greater concentrations at Strumpshaw Fen (Figure 26) resulting in greater CO_2 emission via R_{eco}. VGA has been shown to control R_{eco} in other peatland environments (Bubier et al., 2003, Riutta et al., 2007b), as it increases the oxidised rhizosphere where there is a greater quantity of labile C for r-strategists to mineralise or a greater VGA increases the amount of root exudates released. It is more likely to be the former in this study as R_{eco} was quantified using dark chambers, thus the potential for root exudate release is minimised as the plants cannot photosynthesise. The greater porewater SRP concentrations (Figure 26) at Strumpshaw Fen may have increased plant growth and resulted in greater VGA (Figure 44) than at Sutton Fen, potentially resulting in a greater oxidised rhizosphere due to the greater VGA and thus greater R_{eco}.

N species also were controlling factors on R_{eco} (H_4). Both NO_3^- and NH_4^+ have been shown to increase CO_2 emission by increasing microbial biomass as there is a greater bioavailability of reactants (NO_3^- and NH_4^+) (Amador and Jones, 1993, Min et al., 2011). However, an increase in both NO_3^- and NH_4^+ have also been shown to reduce R_{eco} by altering the pH, and limiting normal microbial function (Aerts and de Caluwe, 1999, Ouyang et al., 2008). PAR was not a controlling factor on R_{eco}. Fluxes were quantified using shrouded chambers, removing the influence of PAR on observed R_{eco}. PAR has been shown to affect R_{eco} in previous studies (Koebsch et al., 2013a) as it is a controlling factor on root exudate release, which can subsequently be mineralised by r-strategist microbes within the rhizosphere.

Dissolved CO_2, DOC and DIC were also significant controlling factors on R_{eco}. DIC and dissolved CO_2 concentrations within the porewater will have an impact on R_{eco} as it alters the concentration gradient between the substrate and the atmosphere, which drives molecular diffusion (Chanton, 2005). DOC has been shown in peat bogs to affect CO_2 efflux, as it is a form of OM that can be mineralised (Moore and Dalva, 2001, Glatzel et al., 2003). pH was also shown to be a controlling factor on R_{eco}. pH has not generally been shown to be a controlling factor on R_{eco} *in situ* in peatlands, as autotrophs are generally specific to their environment. CO_2 production usually increases with pH when

less than pH 7 and decreases when greater than pH 7 (Yiqi and Zhou, 2010). However, a decrease in pH reduces CO_2 solubility within water and encourages degassing of CO_2 (Hope et al., 1995). Additionally, a decrease in pH can be an indication of an increase in NH_4^+ concentrations, which have been shown to aggravate microbes and reduce heterotrophic respiration (Amador and Jones, 1993, Le Mer and Roger, 2001). pH values ranged from 4.3 to 8.3 and 4.7 to 8 for Sutton and Strumpshaw Fen, respectively. Barometric pressure had a relative importance of 93 % and has been shown to induce active transport of CO_2 via aerenchyma in *P. australis* (Armstrong et al., 1992, Brix et al., 1996, Chanton, 2005). Pressure differences between the rhizosphere and atmosphere drive gas movement across the gradient (Chanton, 2005).

4.4.3.2 GPP controlling factors

Air temperature, PAR, VGA, water level and SRP were found to be significant controlling factors on GPP at Sutton and Strumpshaw Fen. Porewater NO_3^- was not, however, a controlling factor as hypothesised. Therefore H_5 was only partially accepted. PAR and VGA were both important controlling factors on GPP at Sutton and Strumpshaw Fen. The relationship between PAR and VGA has an important role on GPP influencing CO_2 assimilation and production of biomass (Kiene and Hines, 1995). Both VGA and PAR have been shown to be a controlling factor on GPP in the literature (Bubier et al., 2003, Kandel et al., 2013b, Koebsch et al., 2013a). These two environmental factors help explain the temporal variation in GPP, with greater uptake during the spring and summer months and little uptake during winter at Sutton Fen. Although VGA was not measured at Strumpshaw Fen during the winter months due to time constraints and land access issues, it was anticipated that values would be zero due to the lack of occurrence of any evergreen plant species. Differences between site's GPP may be caused by differences in plant species composition, with Sutton Fen having a larger abundance of sedges (*Carex spp.*) and evergreen species (*C. mariscus* and *J. subnodulosus;* Figure 45) than at Strumpshaw Fen, which is dominated by *P. australis* (Figure 47). Unfortunately, light-use efficiency has not been studied in the two evergreen species occurring in Sutton Fen (*C. mariscus* and *J. subnodulosus*); however, evergreen species have been shown in other environments to be less efficient at photosynthetic uptake than non-evergreen species due to differences in molecular mechanisms for photosynthesis developed by evergreen species to cope with winter (Gamon et al., 1997, Öquist and Huner, 2003).

Air temperature and water level have been shown to be controlling factors on GPP due to temperatures altering photosynthetic activity, as observed in Syed et al. (2006), and

putting stress on plants with high and low water levels (Riutta et al., 2007b, Koebsch et al., 2013a). SRP has not been shown to affect GPP in the peatland literature; however, it has been shown to increase aboveground biomass (Nykanen et al., 2003, Zhang et al., 2007). The lesser porewater SRP concentrations at Sutton Fen (often < LOD), may account for the smaller VGA (Figure 44) at the site, resulting in the lesser uptake of CO_2 via GPP (Figure 42). NO_3^- was hypothesised to be a controlling factor on GPP (H_5) as it has also been shown to increase aboveground biomass (Nykanen et al., 2003, Zhang et al., 2007). However, NO_3^- was not a controlling factor at Sutton and Strumpshaw Fen, corroborating with Audet et al. (2013a).

Electrical conductivity, relative humidity and pH were found to be controlling factors on GPP, despite not being hypothesised. Electrical conductivity is not a specific measure of porewater chemistry and does not elucidate a true controlling factor on GPP, although it does give light to the total ionic status of the porewater and may highlight areas of further investigation. Relative humidity has been shown in the past to affect photosynthesis by altering stomatal conductance and CO_2 uptake (Aphalo and Jarvis, 1991). More recently, water vapour saturation deficit has been shown to better describe stomatal responses to humidity (Aphalo and Jarvis, 1991, Monteith, 1995). pH has not been shown to be a controlling factor in lowland fens previously. pH does, however, regulate plant species occurrence depending on the species tolerance (Grime et al., 2007). If a plant is taken out of its tolerance, it can put the plant under stress and affect GPP. pH is more likely to be an indicator of changes in nutrient status and the production of phytotoxins from the reduction of certain species (Lund et al., 2010).

4.4.3.3 CH_4 emission controlling factors

Peat temperature, VGA, water level, barometric pressure, NO_3^- and SRP were found to be controlling factors on CH_4 emissions from Sutton and Strumpshaw Fen. Fe^{2+}, as a proxy for redox conditions, was not found to be a controlling factor; therefore, H_6 was only partially accepted. Peat temperature as a controlling factor on CH_4 was consistent with other studies in lowland fens, as an increase in peat temperature increases microbial activity (Schrier-Uijl et al., 2010b, Audet et al., 2013b, Trudeau et al., 2013, Minke et al., 2014). Water level was hypothesised as a controlling factor (H_6) as it is vital for creating anaerobic conditions for methanogenesis to occur and has been observed in a number of studies (Huth et al., 2012, Audet et al., 2013b, Koch et al., 2014). Additionally, water level influences the amount of oxygen diffusion into the peat substrate and consequently regulates the balance between methanogenesis and methanotrophy (Audet et al.,

2013b). A decrease in water level would result in a reduction in CH_4 emissions due to a lesser portion of the peat profile being anoxic for methanogenesis and a great oxic portion of the peat profile for methanotrophy to occur. Water level may not be as important as in other studies (Audet et al., 2013b) due to the deep peat at both Sutton and Strumpshaw Fen, potentially producing CH_4 at depth and it being transported towards the surface via diffusion. pH was not anticipated (H_6) as the difference in pH between the two sites was not thought to be significant and different sites yield differing results for pH (Segers, 1998, Whalen, 2005), despite methanogens being known to be neutrophillic (Koebsch et al., 2013b). The variation in pH between the two sites and the temporal variation must help to regulate differences between Sutton and Strumpshaw Fen and temporal variation in fluxes.

Wind speed cannot be a direct controlling factor on CH_4 emission due to wind speeds in the chamber being less than those measured by the automatic weather station (AWS), a caveat of the method. Studies by Brix et al. (1996) and Armstrong et al. (1992) have shown that wind velocity has an impact on convective through flow of gases (active transport of gases, section 2.3.2) and aerenchymatous plants. Pressure differences develop between the top of the vegetation and the rhizosphere, driving the flow of oxygen into the rhizosphere and CH_4 out into the atmosphere (Armstrong et al., 1992, Brix et al., 1996). This pressure differentiation can be caused by either thermal transpiration or from humidity differential across a leaf boundary (Chanton, 2005), driven by incoming solar radiation. It is more likely that wind speed is an indicator of atmospheric boundary conditions, rather than the direct causal factor on CH_4 emission. Studies in pressure differences between the top of the vegetation and the rhizosphere are not feasible *in situ* without disturbing the substrate and impacting on GHG exchange. Wind speed, however, can be used as a proxy for the atmospheric boundary conditions. Suyker et al. (1996) observed that wind speeds < 1.5 m s^{-1} had an impact on CH_4 emission from a boreal fen, yet speeds > 1.5 m s^{-1} had not impact. This pattern in Suyker et al. (1996) may be a function of boundary conditions, as it would be assumed from research by Brix et al. (1996) and Armstrong et al. (1992) that greater wind velocities would result in greater CH_4 emissions, although Suyker et al. (1996) did not attribute the relationship to atmospheric boundary conditions.

The importance of NO_3^- and SRP on controlling CH_4 emission has been shown before in a number of different studies (Bodelier, 2011, Audet et al., 2013b). The two macronutrients increase plant growth and release C-compounds which may stimulate

methanogenesis (Bodelier, 2011, Audet et al., 2013b). In this study, porewater NO_3^- and SRP concentrations were low throughout the 16 month sampling period and could account for the low relative importance (Table 33). A number of studies have shown the importance of vegetation cover as a controlling factor on CH_4 emission (Koelbener et al., 2010, Koebsch et al., 2013b, Koch et al., 2014). An increasing cover of aerenchymatous plants has been shown to increase CH_4 emission as there are a greater number of aerenchyma to transport CH_4 to the atmosphere (Koelbener et al., 2010). Additionally, a greater cover of *P. australis* allows for greater convective through flow (Armstrong et al., 1992, Brix et al., 1996, Koch et al., 2014). Fe^{2+}, a proxy for redox conditions, was not a controlling factor on CH_4 emission in this study, despite being hypothesised as one (H_6). Audet et al. (2013b) also found that using Fe^{3+} as a proxy for redox conditions was not a controlling factor on CH_4 emission.

Relatively few studies have found electrical conductivity as a controlling factor on CH_4 emission, as it is a measure of total ionic charge and is not provide information on the chemistry of the water. Generally, most studies have looked at specific ions, such as the effect of SO_4^{2-} (Dise and Verry, 2001, Gauci et al., 2005, Audet et al., 2013b), DOC/DIC (Worrall et al., 2005), or NO_3^- (Min et al., 2011). Electrical conductivity was shown to be significantly negatively correlated with ditch CH_4 evasion from a Dutch floodplain fen (Schrier-Uijl et al., 2010b). However, no other chemical analyses were undertaken in the study.

4.5 Summary and synthesis

This chapter sought to quantify *in situ* GHG exchange in two floodplain fens and their ditches over a 16 month sampling period (R.Q.2) and to elucidate the controlling factors on C exchange within the two sites using mixed effects linear modelling (R.Q.3). Fen R_{eco} and NEE varied between sites and over the 16 month sampling period. Observed NEE altered from being similar at both sites in 2012 to Strumpshaw sequestering more CO_2 in 2013. Alterations to VGA from flooding of the two sites at the beginning of the growing season in 2013 is thought to be one of the main driving factors for this difference in NEE between the two years, as VGA was found to be a controlling factor on R_{eco} and GPP (Table 33). Observed R_{eco} was not different between sites and did not show as much of a difference between 2012 and 2013 as NEE. Lower water levels in August and September 2013 to the previous year resulted in greater fluxes than the previous 14 months. Water level was shown to be a significant controlling factor on R_{eco} (H_4).

Ditches at both sites were a source of CO_2 throughout the 16 month period, apart from in April, June and July 2013, where they sequestered a small amount of CO_2. Ditch CO_2 evasion was a significant source of CO_2, despite generally being an order of magnitude less than fen R_{eco}. CH_4 emissions followed a seasonal trend at both Sutton and Strumpshaw Fens (Figure 51 and 52), with ditches emitting the most amount of CH_4 at both sites. CH_4 evasion was generally an order of magnitude greater than fen CH_4 emissions and the majority of CH_4 at both sites was emitted during the summer months. The effects of the March 2013 flood event are seen within the fen CH_4 emission as well as CO_2 exchange (section 4.3.1), with fen CH_4 emission significantly less in 2013 than 2012 at Sutton Fen. Porewater NO_3^- and SRP were also shown to be controlling factors on R_{eco}, GPP and CH_4 fluxes (H_{4-6}). Winter flood events at Sutton and Strumpshaw Fen illustrate the importance of timing, duration and chemistry of site fluvial inundation. The occurrence of flood events before the start of the growing season can result in an increase in C emissions. However, the occurrence at the beginning of the growing season, along with a saline pulse, can have a negative impact on plant growth and microbial processes, subsequently having an effect on C dynamics.

H_{4-6} were partially accepted as mixed effects linear modelling revealed that PAR porewater NO_3^- and porewater Fe^{2+} (a proxy for redox conditions) were not controlling factors on R_{eco}, GPP and CH_4 fluxes, as hypothesised. All other hypothesised controlling factors were shown to be controlling factors (Table 33). Knowing how inundation of floodplain fens can impact on vegetation and C dynamics and what are the controlling factors on C exchange, sites can be managed accordingly to mitigate negative effects on vegetation and reduce C emissions. Additionally, understanding how nutrients increase microbial activity and C mineralisation, agricultural policy on nutrient use can be altered to try to reduce C emissions to the atmosphere from floodplain fens.

5. Methane emission via ebullition in floodplain fen sites of contrasting nutrient status

5.1 Introduction

This chapter reports episodic CH_4 emissions via ebullition from Sutton and Strumpshaw fens from 18th June 2012 to 6th September 2013 and addresses R.Q.4 using the following hypothesis:

H_7: Averaged hourly episodic ebullition rates will be greater at Strumpshaw Fen.

Strumpshaw Fen, the more nutrient enriched site (section 3), will produce more CH_4 due to the greater availability of reactants, which will be transported to the atmosphere via ebullition.

The methods used to quantify ebullition are described in section 5.2. Then ebullition rates and controlling factors on ebullition are presented in section 5.3. Section 5.4 discusses ebullitive rates and contextualises them within the literature. Finally, section 5.5 summarises and synthesises the findings.

5.2 Methodology

As part of R.Q.4, ebullition rates were monitored between 18th June 2012 and 6th September 2013 at Sutton and Strumpshaw Fen. There are few methods that can quantify ebullition due to its episodic nature; however, Strack et al. (2005) created a method whereby a water-filled inverted funnel collects gas over a specific time period, with the gas bubbles displacing the water in the funnel when released. The change in volume of trapped gas in the funnel provides a measure of ebullition over time (Stamp, 2010). The design of the funnel used is based on funnel traps used by Stamp et al. (2013) at Cors Fochno lowland bog, Wales. At Sutton and Strumpshaw Fen, funnel-traps were constructed out of glass with a wall thickness of 3 mm to reduce gas permeability through the funnel walls. A 200 mm diameter funnel was used to give a large basal area. The spouts were replaced (by a glassblower) with 36 x 100 mm lengths of glass tubing and a 250 mm length of 1 mm graduation tape was fitted to the side of the funnel (Figure 62). Rubber bungs with a basal area of 35 mm were used to seal the funnel. A hole was drilled at the top of the funnel and a three-way valve was fitted using aquarium grade silicone sealant (Dow Coring) to form a gas tight seal. Seals were tested thoroughly prior to and throughout the sampling period. The valve served as a sampling port to extract

accumulated gas from when enough gas had collected. Funnels were wrapped in a reflective shroud to minimise solar heating, leaving an observation window for measurement of water height.

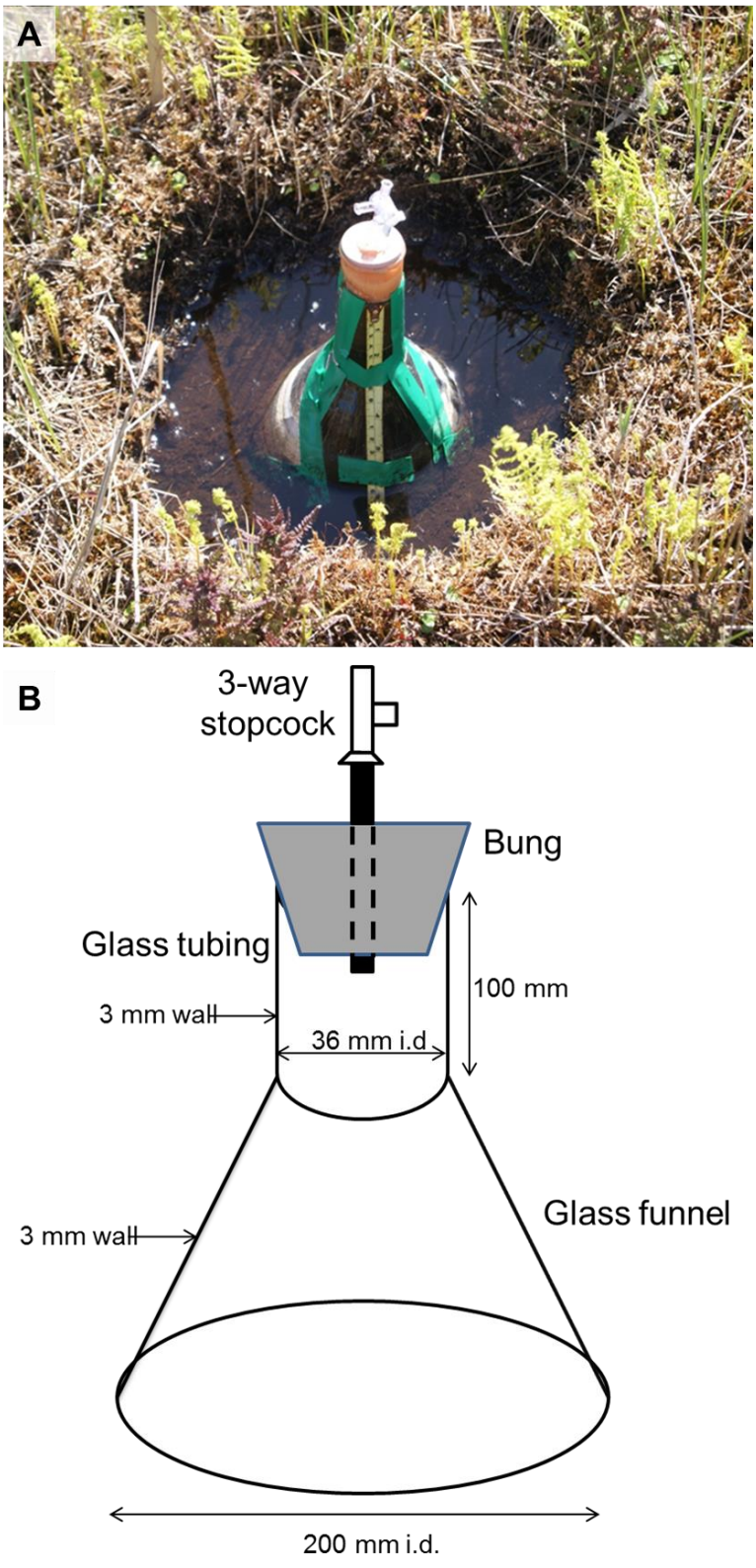


Figure 62 Ebullition funnel trap installed in peat (A) and a schematic of the funnel trap (B).

5.2.1 Location of ebullition funnel traps.

Funnel traps were located within a 2 m radius of each collar at both sites (*n* = 6 per site). Due to the high ebullition rates within the two sites, an additional 6 funnels were added at both sites to help investigate ebullition rates (*n* = 12 per site) from March 2013 onwards. On initial installation of the funnels, a 0.15 m deep hole was cut, with a radius of 0.3 m, using a knife and scissors. Peat was removed carefully, ensuring not to pull out any roots, which were cut. The funnels were installed ensuring that the observation window faced north to prevent creating a microclimate due to solar irradiation. The funnels were filled with water by drawing out air in the trap and allowing it to fill with water from the peat column or an adjacent reservoir. The initial depth of the funnels was found to be too shallow as during summer 2012, as the water level fell below 0.15 m (Figure 32). Thus, the second batch of funnels were installed to a depth of ~ 0.4 m in March 2013 and the first batch of funnels were reinstalled to 0.4 m depth.

5.2.2 Measuring ebullition fluxes.

To investigate R.Q.4, ebullition gas samples were sampled monthly between 9:00 and 17:00 (GMT). It was found that during the summer months, funnel traps were filling up at a faster rate than anticipated and were full before the next sampling date. It was decided that from March 2013 two sampling times would be used to ensure accurate ebullitive rates were calculated: a 24-48 hour sampling period and a 28-30 day period, with funnels left to bubble between visits.

To sample the funnels, firstly the funnel gas volume was measured from a distance of over 2 m using binoculars. The funnel gas was then sampled using a 20 mL disposable syringe via the three-way valve. A 15 mL sample was transferred to a 12 mL pre-evacuated exetainer (Labco Limited). The samples were then stored and analysed using GC-FID fitted with a methanizer (see section 3.2.6.2). The funnels were then left to bubble again, noting the time and date of sample collection and the atmospheric temperature and barometric pressure using a Commeter (C4141, stated manufacturer's accuracy of ± 0.4 °C and ± 0.01 kPa). When working near the funnels, care was taken to stay as far away as possible to reduce disturbance.

5.2.3 Calculating ebullition gas volume

To calculate ebullition rates to the atmosphere, field measurements of funnel-gas (mm) were converted in to a volume of gas (mL). For gas accumulated within the measurement

tube (≥ 60 mm), the relationship was $y = 1.0179x$. For funnel gas measurements ≤ 60 mm, the relationship was different due to the conical shape of the funnel and the funnels were calibrated (Figure 63). An exponential response was found for all funnels (Figure 63), $y = 17.411^{0.0217x}$ and $y = 15.39^{0.0233x}$ for the first and second set of funnels, respectively.

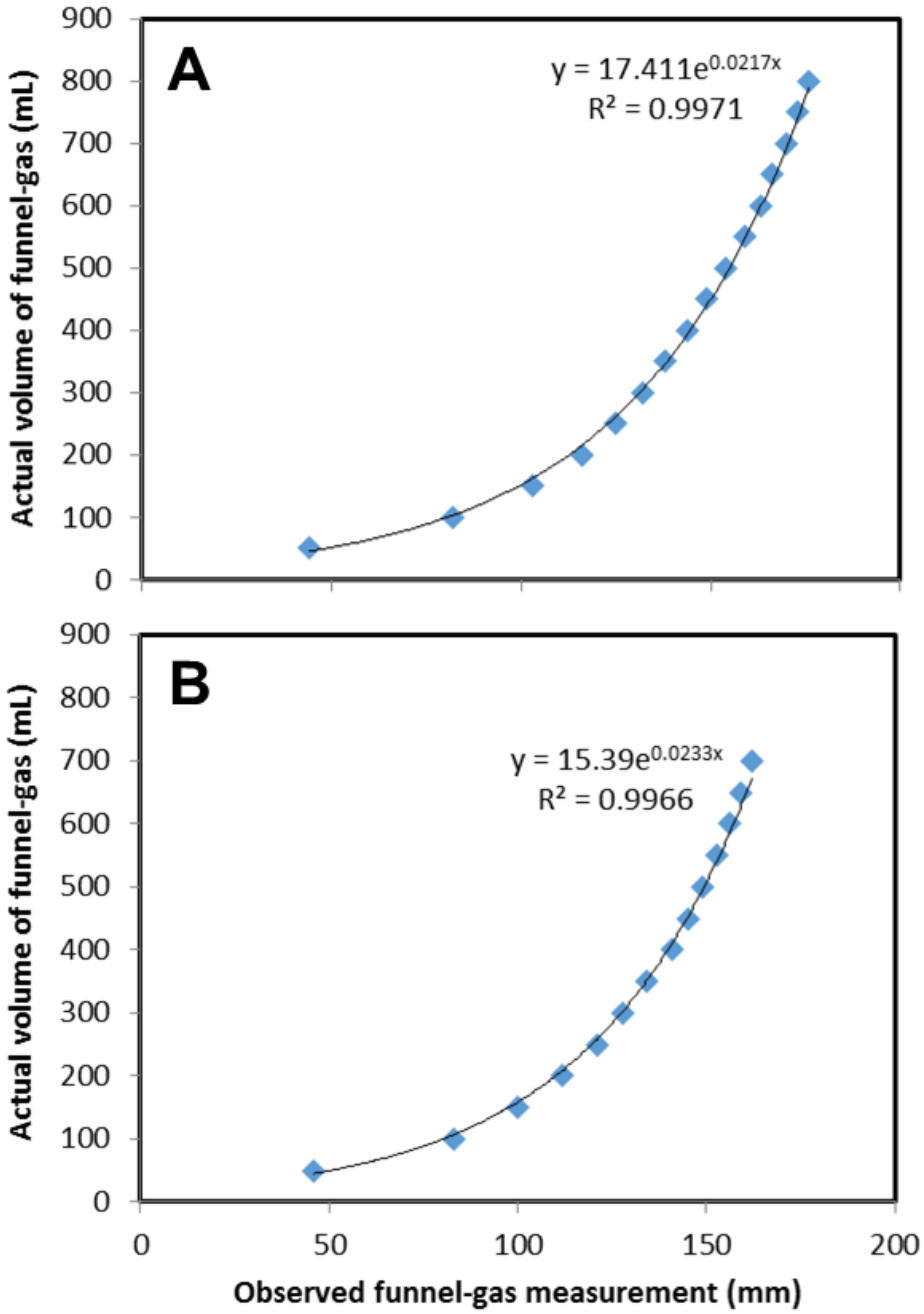


Figure 63 Funnel gas calibrations: relationship between observed funnel gas measurement (mm) and actual funnel gas volume (mL) for the first (A) and second (B) sets of funnels.

5.2.4 Calculating ebullition fluxes

To calculate an hourly average rate of CH_4 ebullition (mg CH_4 m^{-2} h^{-1}; Eq. 19) into the gas funnels, the following measurements are required: (i) the change in funnel gas volume over the measurement period (L), duration of the measurement period (hours), basal area of the funnel trap (m^2), field temperature (°C) and pressure (kPa) measurements, and an estimated CH_4 concentration (Stamp et al., 2013).

Firstly, the change in funnel gas volume for each measurement period was converted into a flux per unit area (Stamp et al., 2013):

$$B_f = \frac{\Delta V_{f-gas}}{A} \quad \text{Eq. 19a}$$

where B_f is the bubble flux (mL m^{-2}), ΔV_{f-gas} is the change in funnel gas volume between the start and end of each funnel run (mL) and A is the basal area of the funnel (m^2).

The volume of CH_4 occupied within the bubbles collected in the funnel trap between measurements was estimated:

$$B_{CH4} = \left(C_{f-gas} \cdot 10^{-6}\right) \cdot \Delta V_{f-gas} \quad \text{Eq. 19b}$$

where B_{CH4} is the volume of CH_4 within the bubbles collected (L), C_{f-gas} is the estimated CH_4 concentration of the funnel gas (ppm), 10^{-6} is a conversion factor for ppm to L and ΔV_{f-gas} is the change in funnel gas volume between the start and end of each funnel run (L).

The volume of B_{CH4} was then corrected using the Ideal Gas Equation:

$$V_{STP} = B_{CH4} \cdot \left(\frac{P_f}{T_f}\right) \cdot \left(\frac{T_{STP}}{P_{STP}}\right) \quad \text{Eq. 19c}$$

where, V_{STP} is the volume of bubble CH_4 at standard temperature and pressure (L), P_f and T_f are field pressure (kPa) and temperature (°C) at the time of sampling, respectively, and P_{STP} and T_{STP} are standard temperature (273.15 K) and pressure (100 kPa), respectively.

The number of moles of CH_4 was then calculated:

$$Mol_{CH4} = \frac{V_{STP}}{Mol_{ig}} \quad \text{Eq. 19d}$$

where, Mol_{CH4} is the number of moles of bubble CH_4 captured by the funnel and Mol_{ig} is the volume of one mole of ideal gas (22.7 L mol^{-1}).

Finally, the hourly average rate of CH_4 ebullition was calculated:

$$F_{CH4} = \left[\frac{Mol_{CH4} \cdot M_{CH4}}{(t_2 - t_1) \cdot A}\right] \quad \text{Eq. 19d}$$

where, F_{CH4} is the average hourly rate of CH_4 ebullition (mg CH_4 m^2 h^{-1}), M_{CH4} is the molar mass of CH_4 (16.04 g mol^{-1}), A is the basal area of the funnel (m^2) and $t_2 - t_1$ is the time between the start of the run and the end (hours).

5.2.5 Controlling factors on ebullitive CH_4 fluxes

Controlling factors on ebullitive fluxes were investigated to further understand differences in ebullitive fluxes between floodplain fen sites of differing nutrient status. Firstly, differences in fluxes between randomly placed funnels and funnels placed next to collars were established. Then controlling factors were elucidated using methods outlined in section 4.2.7 for relative importance of each controlling factor using linear mixed-effects models (Klapstein et al., 2014). Potential independent variables are outlined in Table 34 and are based on results from previous studies (Kellner et al., 2006, Waddington et al., 2009, Klapstein et al., 2014, Yu et al., 2014).

Table 34 Independent variables for ebullitive CH_4 fluxes controlling factors analysis

CH_4 release via ebullition
Average daily barometric pressure
Fall in barometric pressure
Minimum barometric pressure
Maximum barometric pressure
3 day average peat temperature
Water level
Porewater dissolved CH_4 concentration
VGA
Porewater pH
Porewater SRP
Porewater NO_3^-
Porewater NH_4^+
Porewater Fe^{2+}
Porewater Cl^-
Porewater SO_4^{2-}
Porewater DOC
Porewater DIC
Porewater electrical conductivity

5.2.6 Statistical analysis

All statistical analysis was undertaken in R version 3.1.1 (R Core Team, 2014). Comparison of volume of bubbles released over the short sampling period and the gas concentrations were performed using Mann Whitney-U tests in the stats package (R Core Team, 2014). Parametric tests were tried but samples could not be normalised. A linear mixed-effects model was used to compare ebullitive fluxes for the short and long run data, respectively, using site as the independent variable, time as the covariate and funnel replicate as the random effect. The lme function in nlme package was used to run linear mixed effects models (Pinheiro et al., 2014). Differences between ebullition fluxes from funnels placed by collars and randomly placed funnels (inserted post March 2013) were quantified using ANCOVA, with site and month as covariates. ANCOVA and Tukey's multicomparison test were conducted using the stats and multcomp packages in R (R Core Team, 2014, Hothorn et al., 2015). Controlling factors on ebullition were quantified using linear mixed effects model as in section 4.2.7. Independent variables for

controlling factors modelling were examined for correlations with the dependent variable using Spearman's rank correlations (rcorr function in Hmisc package (Harrell and Dupont, 2015)). Relative importance of controlling factors were established using the importance function in MuMIn (Barton, 2014). Comparisons between total porosity at Sutton and Strumpshaw fens were performed using a linear mixed-effects model, with core replicates as a random effect using lme function (Pinheiro et al., 2014).

5.3 Results

5.3.1 Observed Ebullition rates

Ebullition from the two sites (Figure 64) was expressed as an average hourly rate per unit area for each time period (mg CH_4 m^{-2} h^{-1}), and was monitored over two different time periods. Initially funnels were left to bubble between sampling visits (approximately 28 days apart; Figure 64A); however, this time period was found to be too long over the summer months as the funnels filled completely with gas before the next sampling visit. Hence, a shorter run of one or two days was added from March 2013 onwards (Figure 64B). Sutton had greater mean ebullition rates for both the long and short runs (1.2 ± 0.4 and 4.6 ± 1.4 mg CH_4 m^{-2} h^{-1}, respectively), compared to Strumpshaw (0.23 ± 0.06 and 1.9 ± 0.49 mg CH_4 m^{-2} h^{-1}). Ebullition rates for the long runs ranged from 0 to 35 and 0 to 3.2 mg CH_4 m^{-2} h^{-1} for Sutton and Strumpshaw, respectively. Shorter runs at Sutton had a larger range than the longer run (0 to 62 mg CH_4 m^{-2} h^{-1}). This was also observed at Strumpshaw (0 to 19 mg CH_4 m^{-2} h^{-1}). Ebullition was not measured at Strumpshaw during the summer months of 2012 (June 2012 to September 2012) due to funnels being installed at a too shallow depth as water levels fell below the anticipated level. Linear mixed effects models (between factors: site; covariate: time, random effect: funnel replicate) showed ebullition was significantly different between sites and months sampled for the short runs ($F_{1,103}$= 4.068, $p < 0.05$; $F_{5,103} = 7.005$, $p < 0.001$, respectively) but not for the longer runs ($F_{1,125} = 1.218$, $p = 0.272$; $F_{6,125} = 8.616$, $p < 0.001$). No significant interactions were observed between the independent variable and the covariate.

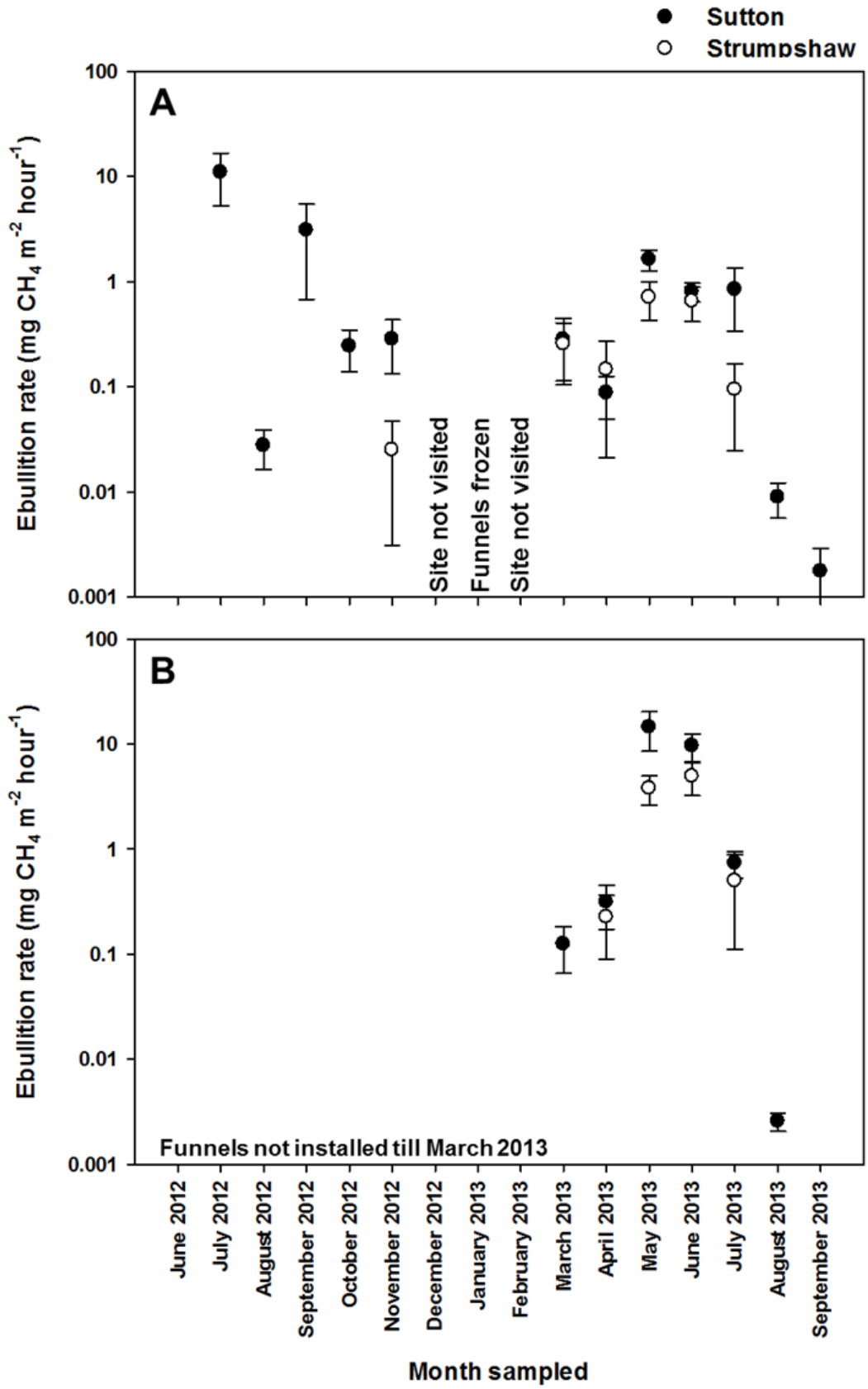


Figure 64 Mean hourly ebullition rates for funnels deployed for 28 days (A) and 48 hours (B) from June 2012 to September 2013 at Sutton and Strumpshaw Fen. Note logarithmic scale. Points represent mean values and error bars denote ± 1 standard error.

There is no clear pattern in ebullition rates for the long run data; however, summer rates are generally greater than spring and autumn rates. Winter rates were not quantified at either site as the sites were not visited in December 2012, nor February 2013. The site was flooded in January 2013 and had frozen over, meaning that funnel gas could not be collected without damaging the funnels. A difference in ebullition data is seen between the two run lengths (Figure 65). Ebullition fluxes from different run lengths have a significant moderate correlation ($r_{108} = 0.68$, $p < 0.001$). This difference between run type is also observed in the ebullition funnel CH_4 concentration (Table 35).

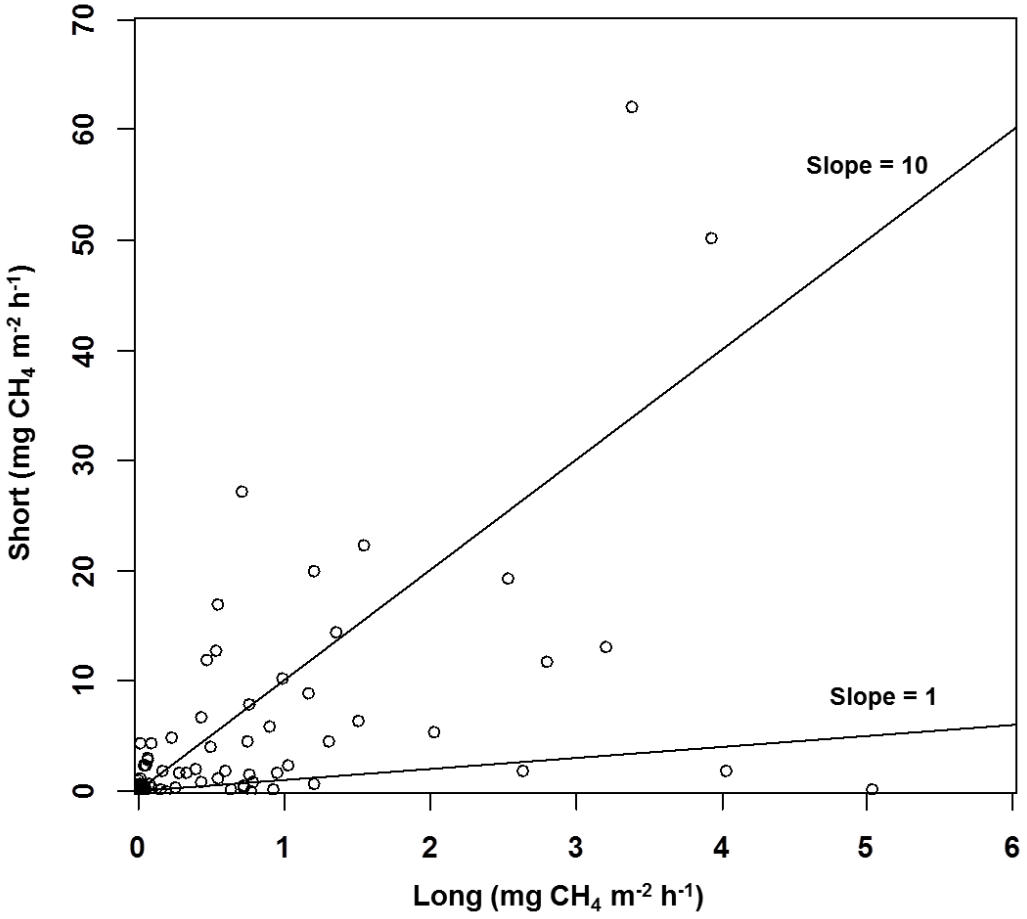


Figure 65 Comparison of 28 day (long) and 48 hour (short) data for ebullition.

Differences in volume of bubble release and concentration of the gas headspace were investigated for the short run. The short run was chosen as CH_4 oxidation by microbes within the aquatic column in the funnel and diffusive movement of CH_4 within the headspace back into the aquatic column would be less than for the longer run. Results showed Strumpshaw had a significantly greater average hourly bubble flux ($U_{263} = 7426$,

$p < 0.05$; 0.12 L m^{-2} h^{-1}) than Sutton Fen (0.09 L m^{-2} h^{-1}). However, Sutton had a significantly greater average funnel concentration ($U_{263} = 11415.5$, $Z = 5.376$, $p < 0.001$; 34757 ± 6504 ppm) than Strumpshaw Fen (8585 ± 2369 ppm).

Table 35 Differences in ebullition funnel CH_4 concentration (mg CH_4 m^{-2} h^{-1}) between short and long runs from April 2013 to September 2013 and the corresponding Mann Whitney-U test.

Month	Short run	Long run	Statistic
April 2013	44709 ± 15996	3459 ± 968	$U_{38} = 103.5$, $Z = -2.518$, $p = 0.018$
May 2013	37828 ± 12185	4193 ± 1051	$U_{44} = 153$, $Z = -2.441$, $p = 0.015$
June 2013	50439 ± 13748	5369 ± 1458	$U_{44} = 84$, $Z = -3.958$, $p < 0.001$
July 2013	96140 ± 31445	1344 ± 952	$U_{44} = 131$, $Z = -2.925$, $p = 0.003$
August 2013	51251 ± 11307	7.1 ± 2.1	$U_{44} = 185$, $Z = -1.737$, $p = 0.042$
September 2013	98 ± 20	48 ± 23	$U_{21} = 6$, $Z = -3.693$, $p < 0.001$

5.3.2 Controlling factors on CH_4 ebullition

Controlling factors on CH_4 release to the atmosphere via ebullition were investigated to help better understand differences in fluxes between floodplain fen sites of differing nutrient status. Firstly, ANCOVA followed by Tukey's multiple comparison test (independent variable: Funnel type, covariate: Site and Month) revealed that there was not a significant difference between ebullition rates in collars placed next to collars and randomly placed collars ($F_{1,262} = 3.1683$, $p = 0.076$). No significant interaction terms between site and depth were observed. Thus funnels placed next to collars were used for controlling factors analysis as collar specific porewater chemistry and environmental data could be used. Controlling factors were established using relative importance, derived from Akaike parameter weights (section 5.2.5). Table 36 shows correlation coefficients for ebullition fluxes and independent variables. Relative importance results are shown in Table 37.

Table 36 Spearman's rank correlation for ebullition flux (CH_4) and selected independent variables (3 day average peat temperature (PT; ˚C), water level (WL; cm above peat surface), average daily barometric pressure (Baro; kPa), the change in minimum pressure between the day prior to sampling and sampling date (Fall; kPa), minimum barometric pressure between sampling (MinB; kPa), minimum barometric pressure between sampling (MaxB; kPa), vascular green area (VGA; m^2 m^{-2}), porewater dissolved CH_4 (AQ; ppm), pH, SRP (mg L^{-1} SRP-P), NO_3^- (mg L^{-1} NO_3^--N), NH_4^+ (mg L^{-1} NH_4^+-N), electrical conductivity (EC; µS cm^{-1}), Fe^{2+} (mg L^{-1}), DOC (mg L^{-1}), DIC (mg L^{-1}), Cl^- (mg L^{-1}) and SO_4^{2-} (mg L^{-1})). * and ** indicate the correlation is significant at the 0.05 and < 0.001 level, respectively.

	CH_4	Baro	PT	Fall	MinB	MaxB	AQ	pH	SRP	NO_3^-	NH_4^+	EC	Fe^{2+}	DOC	DIC	Cl^-	SO_4^{2-}	WL
CH_4																		
Baro	**-0.21**																	
PT	**-0.46****	**0.55****																
Fall	**-0.29***	**0.24***	**0.15**															
MinB	**-0.2**	**0.9****	**0.53****	**0.11**														
MaxB	**-0.14**	**0.85****	**0.57****	**-0.2***	**0.82****													
AQ	**0.13**	**-0.15**	**-0.07**	**-0.1**	**-0.09**	**0.06**												
pH	**0**	**0.27***	**0.08**	**-0.3*2**	**-0.31***	**0.06**	**0.04**											
SRP	**0.3***	**0.06**	**-0.28***	**0.24***	**0.04**	**0.03**	**0.24***	**-0.26***										
NO_3^-	**0.23***	**-0.49****	**-0.52****	**-0.07**	**-0.52****	**0.54****	**0.01**	**0.04**	**0.34***									
NH_4^+	**-0.05**	**0.13**	**0**	**0.06**	**0.07**	**0.08**	**-0.05**	**-0.02**	**-0.18**	**0.24***								
EC	**-0.2***	**0.31***	**0.37****	**0.37****	**0.28***	**0.24***	**0.23***	**0.08**	**0.5****	**-0.06**	**-0.31***							
Fe^{2+}	**0.05**	**-0.14**	**-0.1**	**-0.24***	**-0.11**	**0.03**	**-0.33**	**-0.02**	**-0.27***	**-0.04**	**0.07**	**-0.53****						
DOC	**0.43****	**-0.28***	**-0.5****	**-0.23***	**-0.33***	**0.27***	**0.05**	**0.21***	**0.1**	**0.46****	**0.21***	**-0.19**	**0**					
DIC	**0.55****	**-0.29***	**-0.68****	**-0.14**	**-0.23***	**0.3***	**0.29***	**-0.09**	**0.39****	**0.22**	**-0.04**	**-0.12**	**-0.05**	**0.44****				
Cl^-	**-0.36***	**0.29***	**0.32***	**0.48****	**0.22***	**0.16**	**0.17**	**0.08**	**0.42****	**0.03**	**-0.23***	**0.9****	**-0.51****	**-0.15**	**-0.23***			
SO_4^{2-}	**-0.23***	**0.23***	**0.07**	**0.32***	**0.14**	**0.11**	**0.01**	**-0.03**	**0.39****	**0.16**	**-0.14**	**0.47****	**-0.48****	**-0.18**	**-0.06**	**0.52****		
WL	**0.46****	**-0.34***	**-0.87****	**0.1**	**-0.32***	**0.49****	**0.09**	**-0.31***	**0.55****	**0.53****	**-0.04**	**-0.12**	**-0.06**	**0.44****	**0.71****	**-0.08**	**0.09**	

Table 37 Relative importance of each controlling variable on ebullitive fluxes.

Parameter	Relative importance
Fall in barometric pressure	0.99
DIC	0.97
Barometric pressure	0.96
Minimum barometric pressure	0.93
Water level	0.89
Electrical conductivity	0.86
Peat temperature	0.86
pH	0.77
NH_4^+	0.70
Cl^-	0.57
Fe^{2+}	0.47
NO_3^{2-}	0.44
DOC	0.40
SO_4^{2-}	0.34
SRP	0.29
Dissolved CH_4	0.24

5.4 Discussion

This chapter investigated intra-annual variability of CH_4 emission from two lowland floodplain fens using the following research question and hypothesis:

R.Q.4. What are the averaged hourly episodic ebullition rates from two floodplain fens of differing nutrient status?

H_7: Averaged hourly episodic ebullition rates will be greater at Strumpshaw Fen than Sutton Fen.

To establish if there was a difference in CH_4 release to the atmosphere via ebullition between sites, ebullitive fluxes were investigated over a 16 month period (18th June to 6th September).

5.4.1 Differences in ebullition between sites of differing nutrient status

Relatively few studies have quantified ebullition from temperate floodplain fens. CH_4 release to the atmosphere via ebullition was found to be significantly greater at Sutton Fen than a Strumpshaw Fen from March 2013 to September 2013. No significant difference in ebullition between sites was observed for the long run data; however, this may be due to the lack of data at Strumpshaw Fen in 2012 due to the funnels being

installed at an incorrect depth. Data was shown to be more reliable from shorter runs, as CH_4 did not diffuse back into the water column as much. Therefore, on the basis of the shorter run data, H_7 was rejected as Sutton Fen had significantly greater ebullition rates.

The difference in ebullition rates observed between Sutton and Strumpshaw Fen (Table 16) may be due to differences in porewater chemistry. Regression analysis showed a number of porewater chemical parameters to be controlling factors on ebullition. No previous study has researched how nutrients affect episodic release of CH_4 to the atmosphere via ebullition, making this study unique. Significant differences in porewater NH_4^+, NO_3^-, SRP and SO_4^{2-} concentrations (Table 16) may also result in lesser funnel CH_4 concentrations at Strumpshaw Fen in comparison to Sutton Fen. Porewater NH_4^+ and NO_3^- were shown to be important controlling factors on ebullition rates (Table 37). The greater concentrations of porewater NO_3^- and NH_4^+ (Figure 26) at Strumpshaw Fen than Sutton Fen may have inhibited CH_4 production as they have been shown to inhibit methanogenesis (section 2.3.4) (Knittel and Boetius, 2009, Smemo and Yavitt, 2011, Gupta et al., 2013). Additionally, the greater porewater SO_4^{2-} concentrations at Strumpshaw Fen may have affected ebullition rates, despite being a lesser important controlling factor (Table 37). SO_4^{2-} reduction can result in the production and emission of volatile sulphur compounds, such as hydrogen sulphide and dimethyl sulphide, potentially increasing the bubble flux from the site in comparison with Sutton Fen. Unfortunately, volatile sulphur compounds were not analysed as part of this study.

Peat structure may also affect ebullition rates between sites, as this can alter bubble residence time and release (Kellner et al., 2006). In peat with small pore sizes, gas bubbles are trapped more easily, allowing gas bubble size to grow with the addition of other bubbles and the stripping of CH_4 from the surrounding porewater, and then released in a sudden outburst (Kellner et al., 2006). In more open pore structures, bubbles are released more readily and frequently as the bubbles are not trapped as easily (Kellner et al., 2006). It is hypothesised that there is a greater amount of pore spaces at Sutton Fen than at Strumpshaw Fen, due to the greater peat bulk density at Strumpshaw Fen (Figure 16A). The greater number of pore spaces at Sutton Fen result in a larger bubble residence time, resulting in a smaller average hourly bubble flux; higher average hourly concentration, as more CH_4 can be stripped form the areas surrounding the trapped bubbles; and greater ebullition rates than at Strumpshaw Fen. Total porosity was calculated (Figure 66) for both sites using bulk density data collected in chapter 3. Results showed a significant difference between sites, especially in the top 0.5 m (Figure

65). Sutton Fen had a significantly higher porosity in the first 0.5 m below the peat surface, whilst Strumpshaw's porosity was lower (Figure 65). Porosity values were within literature values for peat (Baldwin and Mendelssohn, 1998, Pagter et al., 2005, Saltmarsh et al., 2006). Values are a measure of total porosity and do not show the pore sizes, which may vary between sites.

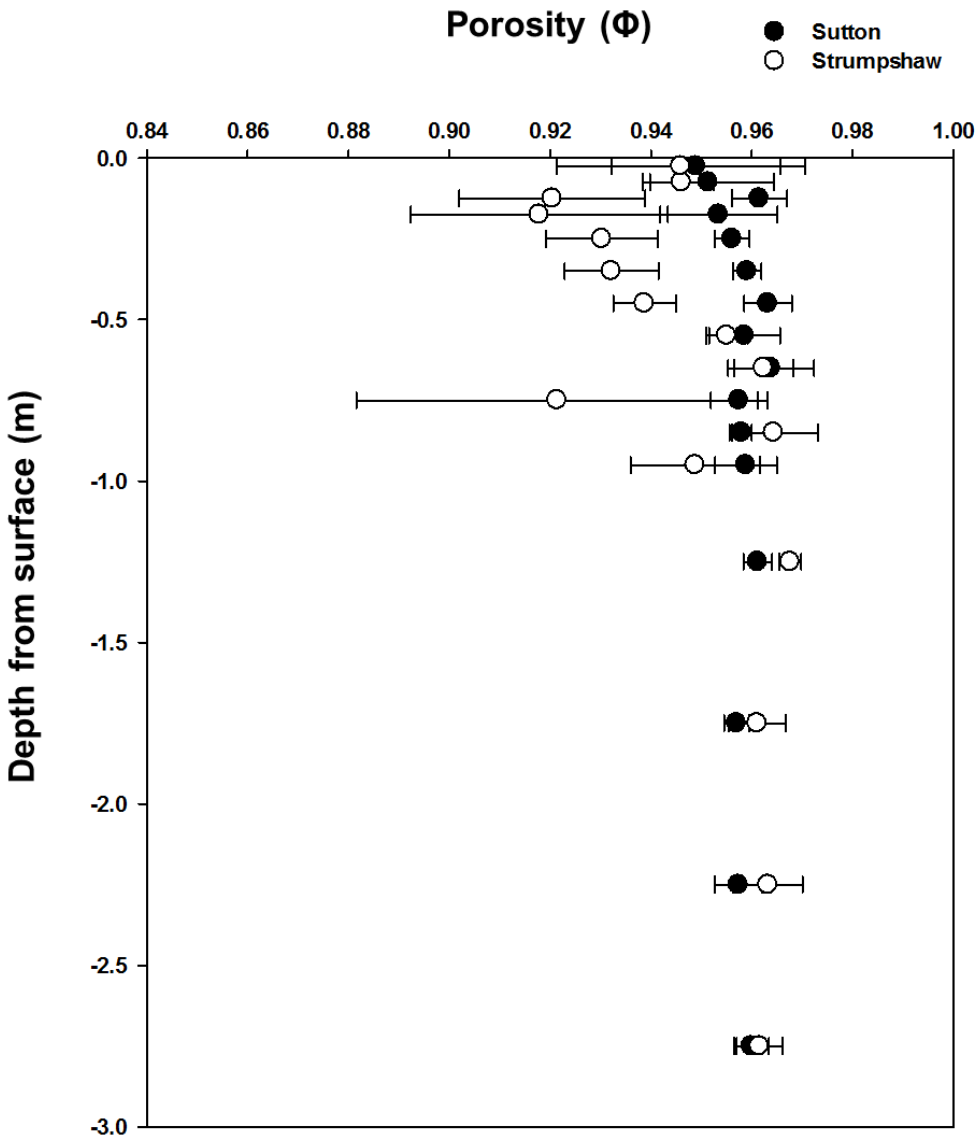


Figure 66 Total porosity values for Sutton and Strumpshaw Fen. Circles represent triplicate core values for each depth and error bars denote ± 1 standard error. A linear mixed-effects model (independent variable: Site, covariate: Depth, random effect: core replicate) showed a significant difference in total porosity between sites ($F_{1,91} = 5.312$, $p = 0.023$) and not depth ($F_{1,91} = 7.179$, $p = 0.008$). No significant interaction terms between site and depth were observed.

The small dense root mat overlying peat at Strumpshaw Fen (Figure 15) and the greater bulk density than at Sutton Fen (Figure 16A) will restrict bubble accumulation within the peat substrate. However, the greater number of dead graminoid culms at Strumpshaw Fen may aide in the transfer of bubbles accumulated in the peat. A number of studies have shown the active venting of gases within *P. australis* vegetation as a means to oxidise the rhizosphere (Brix, 1989, Armstrong et al., 1996, Brix et al., 1996). It is possible the pressure differential between the top of the culm and the peat may induce episodic ebullition and promote steady ebullition. Two of the greatest diffusive and plant-mediated fluxes observed in chapter 4 using static chambers (Figure 48) were at Strumpshaw Fen and were thought to potentially be due to steady ebullition events (section 2.3.2) as the fluxes were an order of magnitude greater than all other diffusive and plant-mediated CH_4 fluxes. However, definitively teasing out steady ebullition events is extremely difficult.

5.4.2 Importance of ebullition as a CH_4 transport mechanism

Ebullition was shown to be an important pathway for CH_4 release to the atmosphere in this study, as fluxes were within a similar order of magnitude to diffusive and plant-mediated fluxes at Sutton and Strumpshaw Fen (Figure 48 and 63). Previous studies have shown ebullition is an important transport mechanism for CH_4 transport to the atmosphere (Rosenberry et al., 2003, Stamp et al., 2013); however no study has shown ebullition to be as an important transport mechanism as diffusive and plant-mediated routes, nor monitoring rates over a whole year. Additionally, no study has ebullition rates over two different sampling periods (< 48 hours, and c. 28 day run). The results from these two different runs follow a similar pattern, with highest rates in May and June 2013 (Figure 63). Interestingly, rates from the shorter run (Figure 63B) are generally an order of magnitude greater than the longer run (Figure 63A; Figure 64). The difference is thought to be due to both methanotrophs oxidising the CH_4 within the funnel traps and the movement of CH_4 via diffusion from the gas headspace in the funnel back into the water column in order to equilibrate the concentration difference between the two. Over a longer sampling time period, these two processes can reduce CH_4 concentration more within the funnel headspace. This is observed in the difference in CH_4 concentration between the two different runs, with the shorter runs having significantly greater CH_4 concentrations (Table 32). Therefore, within these environments where frequent ebullition occurs, a shorter sampling period of 48 hours to capture ebullition gives more reliable results. With a shorter sampling period there is less time for movement of CH_4 out of the funnel and for methanotrophs within the aquatic column in the funnel to oxidise the gas headspace. This sample frequency may not be suitable for other environments

where ebullition events are not as frequent or during months when bubble frequency is reduced, such as during the winter months.

Until recently, ebullitive fluxes had not been properly accounted for in peatland studies (Coulthard et al., 2009). A number of laboratory (Tokida et al., 2005, Kellner et al., 2006, Green and Baird, 2012) and field based studies (Rosenberry et al., 2003, Strack and Waddington, 2008, Stamp et al., 2013) have tried to quantify ebullition within different peatland systems (Figure 63), showing the importance of this mechanism for CH_4 emission to the atmosphere (Stamp et al., 2013). Stamp et al. (2013) measured ebullition in two microhabitats at Cors Fochno, a patterned raised bog in Wales. The authors found that ebullition funnels usually bubbled for at least one week during the study, remaining dormant for the rest of the time. This dormancy was not observed at Sutton and Strumpshaw Fen, where ebullition occurred frequently over the spring, summer and autumn months. When Sutton Fen was visited in January 2013 gas was present within the funnels; however, they were not sampled during this time due to water in the funnels being frozen. Fluxes to the water table varied greatly at Cors Fochno, with fluxes ranging between 0 to 24 mg CH_4 m^{-2} h^{-1} (based on weekly readings expressed as an hourly averaged flux; Stamp et al., 2013). The range at Sutton Fen (0 to 35 mg CH_4 m^{-2} h^{-1}) was greater than at Cors Fochno, yet less at Strumpshaw Fen (0 to 3.2 mg CH_4 m^{-2} h^{-1}). A difference between the studies was expected due to the difference in peatland type. Mean ebullitive fluxes from Strumpshaw were more similar to fluxes from a poor fen near St. Charles-de-Bellchasse, Québec, Canada, where Strack et al. (2005) reported a mean ebullitive flux of 2.7 mg CH_4 m^{-2} h^{-1} and a range of 0 to ~ 4.7 mg CH_4 m^{-2} h^{-1}. Mean ebullitive flux from Sutton (2.5 ± 0.6 mg CH_4 m^{-2} h^{-1}) and Strumpshaw (0.9 ± 0.2 mg CH_4 m^{-2} h^{-1}) were less than the mean at St. Charles-de-Bellchasse (Strack et al., 2005). Ebullition from both Sutton and Strumpshaw Fen was within the literature values (Figure 67).

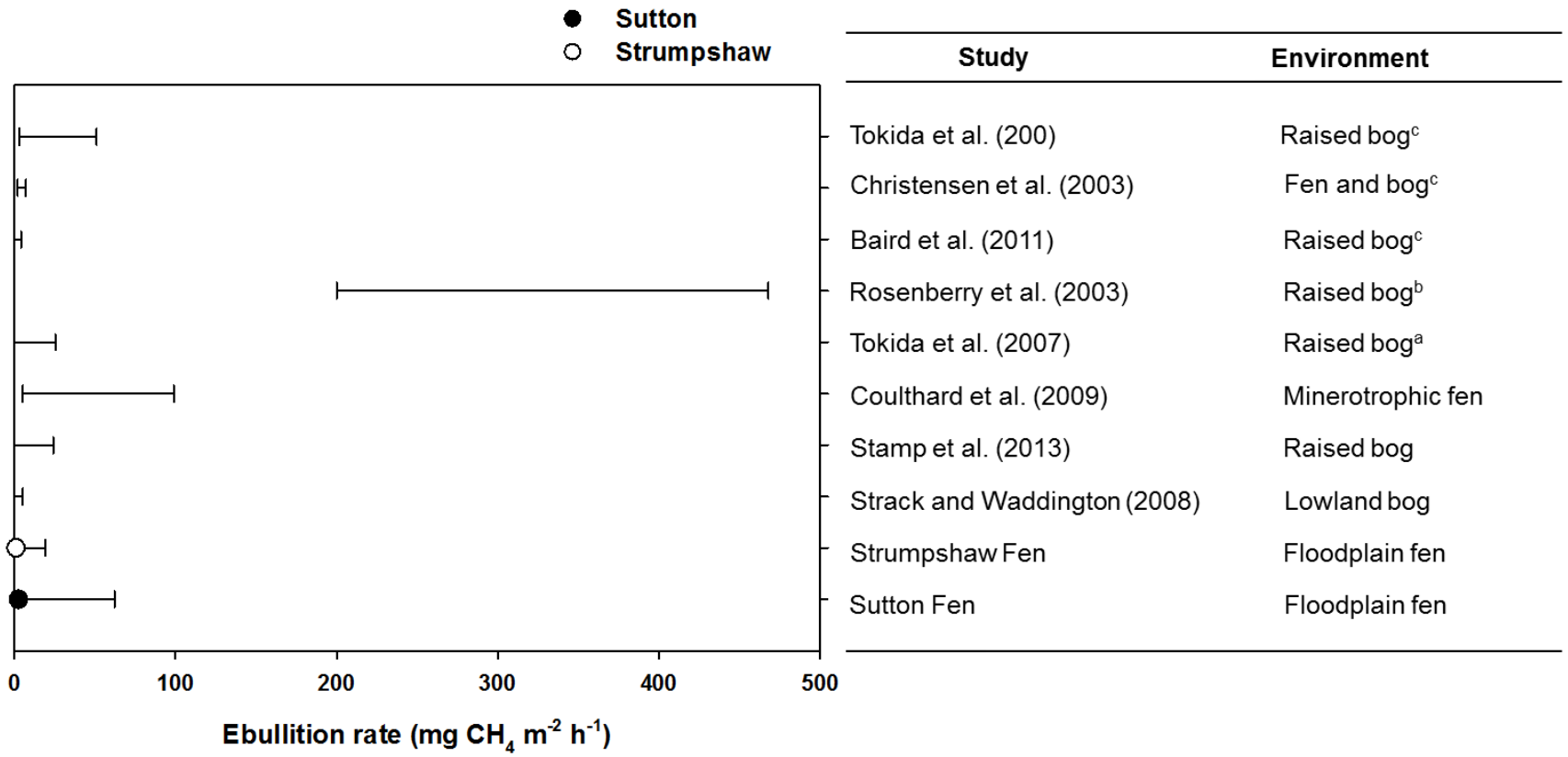


Figure 67 Comparison of literature ranges in ebullition rates and Sutton and Strumpshaw Fen using ebullition funnels unless stated otherwise (a = needle and syringe extraction of gas from a frozen water surface, b = hydraulic head method, c = *ex situ* mesocosm experiments). Points represent mean values and bars denote minima and maxima values.

5.4.3 Controlling factors on ebullition

Controlling factors on CH_4 release to the atmosphere via ebullition were investigated to help better understand differences in fluxes between sites. Results presented in Table 37 showed the fall in minimum barometric pressure between the previous day and the day of sampling to be the most important controlling factor on ebullition rates. Decreases in atmospheric pressure has been shown to destabilise structural stability of free-phase bubbles and induce bubble release (Klapstein et al., 2014, Yu et al., 2014). This strong relationship between the change in atmospheric pressure and ebullition rates (Table 37) was also observed in Klapstein et al. (2014) and Yu et al. (2014). Barometric pressure was not found to be as important as the fall in minimum barometric pressure within this study (Table 37), as in other studies (Fechner-Levy and Hemond, 1996, Kellner et al., 2006, Waddington et al., 2009, Yu et al., 2014).

Water level was found to be a more important controlling factor than barometric pressure (Table 37). Changes in water level will affect pressure and can bubble volumes to change following the ideal gas law. Additionally, changes in water level will also adapt the oxic/anoxic portions of the peat profile and consequently areas where methanogenesis can occur (Fechner-Levy and Hemond, 1996, Segers, 1998).

Unlike in other studies (Fechner-Levy and Hemond, 1996, Klapstein et al., 2014, Yu et al., 2014), peat temperature was an important controlling factor on ebullition (Table 37). Temperature alterations will affect both bubble volume through the ideal gas law and gas concentration, as gas solubility in water reduces with increases in temperature (Yamamoto et al., 1976, Kellner et al., 2006, Strack and Waddington, 2008, Klapstein et al., 2014). Increases in temperature will also increase rates of methanogenesis, as microbial activity has been shown to increase with temperature (Andersen et al., 2013). Funnel bubble volume was found to be a more important controlling factor on ebullition than funnel gas concentration. The greater importance of funnel bubble volume than concentration may be due to the triggers that induce ebullition. An increase in gas concentration within a free-phase gas bubble does not necessarily result in the destabilisation of the bubble within a pore space and the subsequent movement towards the atmosphere. An increase in bubble volume can induce bubble destabilisation and transport to the atmosphere.

Porewater chemistry also influenced ebullition rates. No previous study has researched how porewater chemistry affects ebullition, making this work unique. DIC and NH_4^+ concentrations were the two most important chemical parameters controlling ebullition (Table 37). Both DIC and NH_4^+ are primarily produced during decompositional processes within floodplain fens. Greater rates of decomposition of the peat substrate within a fen would result in greater rates of free-phase CH_4 production and subsequently gas accumulation and emission to the atmosphere. Dissolved CH_4 concentrations were not as important a controlling factor (Table 37) due to CH_4 being sparsely soluble in water (Yamamoto et al., 1976). Porewater NO_3^- and SRP concentrations were controlling factors on ebullition (Table 37), as they provide reactants to methanogens to help increase microbial biomass and augment production rates.

5.5 Summary and synthesis

In summary, the 16 month sampling period provides evidence of the importance of ebullition as a CH_4 transport mechanism to the atmosphere. Ebullition rates were significantly greater at Sutton Fen than Strumpshaw Fen over 48 hours, resulting in H_7 being rejected. Differences in ebullitive rates were observed between sites and corroborated with diffusive and plant mediated fluxes reported in section 4.3.4. Ebullition rates were found to be within a similar order of magnitude to terrestrial plant-mediated and diffusive fluxes (section 4.3.4; Figure 48), illustrating the importance of this transport mechanism within these two sites. Differences in ebullitive rates were also observed between the two sampling times (28 days and 2 days), with shorter runs giving more representative fluxes in floodplain fens. Taking this finding into account, future research designs for ebullition studies can be scaled appropriately for the type of environment being studied and how frequently bubble traps are sampled. As seen in this study and other ebullition studies (Strack et al., 2005, Stamp et al., 2013), ebullition fluxes are highly spatially and temporally variable and further work is needed in small spatial scale variability in ebullitive fluxes and on the mechanisms controlling ebullition events.

Regression analysis revealed the fall in minimum barometric pressure between the previous day and day of sampling to be the most important controlling factor on ebullition and corroborates with other studies. Peat temperature and water level were also other important controlling factors. This study also showed the importance of porewater chemistry on ebullition, which has not previously been shown in the literature. Understanding the controlling factors on ebullition, floodplain fen sites can be managed accordingly to try to reduce CH_4 emissions to the atmosphere.

6. Annual carbon exchange from floodplain fen sites of contrasting nutrient status

6.1 Introduction

This chapter reports annual carbon (C) exchange from two floodplain fens of differing nutrient status (section 3.3) based on data from section 4.3, as well global warming potentials (GWP) and the relative contribution of aquatic and terrestrial CH_4 emissions for Sutton and Strumpshaw Fen. The following research questions (R.Q.) and hypotheses (H) will be answered within this chapter:

R.Q.5. Over a one year period, what are the integrated annual fluxes for CO_2 and CH_4 from the two floodplain fens?

H_8: Strumpshaw Fen will have greater annual fluxes for GPP, R_{eco} and CH_4.

The greater N and P contents/concentrations observed in the vegetation, surface peat and porewater at Strumpshaw Fen than at Sutton Fen (section 3.3) will result in greater aboveground green biomass at the nutrient enriched site and subsequently, greater GPP. Aboveground biomass has also been shown to be correlated with root exudate release into the rhizosphere (Ström et al., 2003). With greater root exudate release into the rhizosphere from the greater aboveground biomass, greater amounts of labile C will be available at Strumpshaw Fen for respiration and methanogenesis (Ström et al., 2003). In addition, respiration and methanogenesis will be enhanced at Strumpshaw Fen due to the greater reactant availability. N and P have been shown to act as reactants and increase respiration and methanogenesis in peatlands (Ouyang et al., 2008).

R.Q.6. What are the CO_2 equivalent GHG fluxes for each GHG for Sutton and Strumpshaw fens?

H_9: CH_4 will have a greater CO_2-equivalent flux than CO_2 at both sites.

Floodplain fens under conservation management often have their water levels managed to help maintain the sites and promote the accumulation of peat. The anoxic conditions that ensue with high water tables promotes methanogenesis and reduces the efficiency of heterotrophic respiration.

H_{10}: Strumpshaw Fen will be a greater sink of C than Sutton Fen.

The greater aboveground biomass at Strumpshaw Fen due to the greater nutrient status at the site will result in greater rates of CO_2 sequestration during the day than CH_4 and CO_2 emissions via autotrophic and heterotrophic respiration combined.

Methods used for infill modelling, CO_2-equivalent flux calculations and estimations of terrestrial and aquatic CH_4 fluxes relative to surface area are presented in section 6.2. Controlling factors analysis on observed fluxes are shown in chapter 4. Section 6.3 presents annual fluxes, section 6.4 outlines CO_2-equivalent fluxes for Sutton and Strumpshaw Fen, and section 6.5 details terrestrial and aquatic CH_4 fluxes relative to surface area. Section 6.6 discusses results and section 6.7 provides a summary and synthesis of the findings.

6.2 Modelling methodology

6.2.1 Infill modelling for C exchange

Infill modelling was done as ecosystem respiration (R_{eco}), net ecosystem exchange (NEE) and CH_4 were not measured continuously throughout the sampling period. Infilling between sampling was therefore needed to calculate an annual flux as part of R.Q.5. Regression analysis is a simple, commonly used modelling approach to derive annual fluxes from momentary fluxes captured using chamber techniques (Laine et al., 2009). In order to calculate annual fluxes for CO_2 (gross primary production, GPP; R_{eco}) and CH_4 (R.Q.5.), in fill modelling techniques were used on the observed data presented in Chapter 4. Specific independent variables had to be chosen which were measured at an hourly interval over the 16 month sampling period to facilitate hourly flux reconstruction. As part of the model construction, independent variables were chosen using expert knowledge (based on literature findings) to enter into the regression models. Furthermore, relationships between independent variables for CO_2 (GPP, R_{eco}) and CH_4 models (Table 38) were investigated using correlation matrices to ascertain correlations between fluxes and their independent variables and if any of the independent variables correlated with each other. If so, variables with a smaller correlation with the dependent variable were removed to reduce collinearity within the final models. Mixed effects generalised linear models (ME GLM; CH_4) and non-linear mixed effects models (ME NLM; GPP and R_{eco}) (Laine et al., 2007a, Laine et al., 2007b, Maanavilja et al., 2011) were used, using the packages lme4 (Bates et al., 2014) and nlme (Pinheiro et al., 2014), respectively. Models were constructed using R 3.1.1 (R Core Team, 2014) and were assessed using the corrected Akaike Information Criteria (AICc), as this allows inter-

model comparison, whilst discriminating for the number of independent variables included (Akaike, 1974, Hurvich and Tsai, 1991). AICc was used in preference over Akaike Information Criteria as AICc accounts for a non-negligible bias when the sample size is not so large (Imori et al., 2013). Furthermore, negative log likelihood (-loglik) was used to assess the quality of the models, as it is a measure of goodness of fit of a model based on observed data and parameter values (Pinheiro and Bates, 1995). As R^2 values cannot be calculated for mixed-effects models, Nash Sutcliffe model efficiency (NSE) coefficients were used to compare observed data and predicted data, based on Eq. 20 (Nash and Sutcliffe, 1970, Krause et al., 2005, Audet et al., 2013b). Model efficiency (MEF) coefficients are a measure of a models predictive power, defined as one minus the sum of the absolute squared differences between the predicted and observed values normalised by the variance of the observed values during the period under investigation (Nash and Sutcliffe, 1970, Krause et al., 2005, Audet et al., 2013b).

$$MEF = 1 - \frac{\sum_{i=1}^{n}(O_i - P_i)^2}{\sum_{i=1}^{n}(O_i - \bar{O})^2} \quad \text{Eq. 20}$$

where MEF is the NSE coefficient (the range in E lies between 1.0, a perfect fit, and $-\infty$, O is observed and P is predicted values.

Models for CH_4, GPP and R_{eco} were then run in an iterative manner of inclusion and exclusion of all independent variables to find the best model. Distribution of residuals of the individual response functions were examined to check for homogeneity and normality to validate model formats (Laine et al., 2007a, Laine et al., 2007b, Maanavilja et al., 2011). Delta AICc values were then compared to establish the best model. Sensitivity analysis of final models was undertaken by varying separately each environmental variable by ± 10 % (Laine et al., 2007a, Laine et al., 2007b, Maanavilja et al., 2011). Using plot specific coefficients and AWS environmental data, hourly GPP, R_{eco} and CH_4 fluxes were estimated for the study period (Laine et al., 2007a, Laine et al., 2007b, Maanavilja et al., 2011). The annual fen R_{eco}, GPP, NEE and CH_4 fluxes were integrated from 1st September 2012 to 31st August 2013. Ditch and ebullitive fluxes were not modelled due to the small number of replicates (ditches) and the lack of data in 2012 (ebullition; section 5.3.1). Calculating annual fluxes based on the ditch and ebullition data would have resulted in unrepresentative fluxes.

Table 38 Independent variables for mixed effect linear and non-linear regressions for infill modelling to calculate annual *GPP*, R_{eco} and CH_4 fluxes.

GPP	R_{eco}	CH_4
Air temperature	Air temperature	Air temperature
Barometric pressure	Barometric pressure	Barometric pressure
Wind speed	Wind speed	Wind speed
PAR	PAR	PAR
VGA*	Substrate temperature at 5 cm below peat	VGA*
Substrate temperature at 5 cm below peat	Substrate temperature at 90 cm below peat	Substrate temperature at 5 cm below peat
Substrate temperature at 90 cm below peat	Water level	Substrate temperature at 90 cm below peat
Water level		Water level

*VGA can be calculated using phenology models already published.

6.2.1.1 CO_2 exchange modelling

In order to calculate annual CO_2 exchange, a multiplicative modelling approach was chosen for GPP and R_{eco} annual reconstructions and models were based on models within the literature for GPP (Kiene and Hines, 1995) and R_{eco} (Kandel et al., 2013a, Kandel et al., 2013b). Multiplicative models are often used when the effects of individual parameters are not differentiated, the seasonal pattern in data depends on the magnitude of the data and the relationship between independent variables and the dependent variable are non-additive (Menzefricke, 1979), as in the case for GPP and R_{eco}. This is especially the case for the relationship between GPP, as if PAR is 0 µmol m^{-2} s^{-1} then no uptake of CO_2 via sequestration will occur. Spatial variation in plant community was acknowledged by including collar as a random effect within the models, as this has been shown to improve model performance (Kettunen et al., 2000, Laine et al., 2007a, Laine et al., 2009).

Firstly, observed NEE was partitioned into light-dependent GPP and light-independent R_{eco} (Kandel et al., 2013a), estimating GPP as R_{eco} – NEE as in Chapin et al. (2006). Independent variables were then checked to see if they were correlated with each other in order to eliminate collinearity. PAR was included as a parameter despite not being significantly correlated to GPP. A shortlist of candidate variables was created (Table 39) with data logged at an hourly interval so as to facilitate infill modelling at an hourly interval.

Table 39 Final independent variables for GPP and R_{eco} infill modelling.

GPP	**R_{eco}**
PAR	Peat temperature
VGA	Water level
Air temperature	VGA
Water level	

VGA was the only parameter not recorded at an hourly interval that was included in the final independent variable list; however, a measure of vegetation green area has been shown to significantly improve R_{eco} and GPP models (Bubier et al., 1999, Riutta et al., 2007a, Kandel et al., 2013b, Koebsch et al., 2013a). Collar specific phenology models

were constructed using nonlinear mixed-effects models, with collar as a random effect to explain variability, to model daily VGA. Individual phenology models per collar could not be constructed due to lack of data (only n = 14 and 12 per collar at Sutton and Strumpshaw Fen, respectively) over the 16 month sampling period. Therefore, the use of a nonlinear mixed-effects model helped to improve the overall fit of the model. A number of different responses were trialled but a unimodal response was used to model daily VGA, with a clearly defined maximum (Eq. 21) as in Wilson et al. (2007a), as it yielded the best AICc value:

$$Daily\ VGA_i = VGA_{max} \cdot e^{\left(-0.5\left(\frac{julian - x_{max}}{b}\right)^2\right)} \quad \text{Eq. 21}$$

where VGA_{max} denotes the maximal VGA of a species, $julian$ is Julian day, x_{max} denotes the Julian day when VGA_{max} occurs and b represents the shape of the curve (Wilson et al., 2007a). VGA_{max}, x_{max} and b are fitted parameters.

GPP and R_{eco} model optimisation was undertaken using an iterative process of inclusion and exclusion of independent variables (Gitzen and Millspaugh, 2012). Additionally, a number of different model structures were tested to optimise the model, including collar as a random effect and site as a fixed effect (different intercept and slope, or same intercept, different slope).

Annual NEE was estimated using Eq. 22 (Chapin et al., 2006). Hourly estimates for R_{eco}, GPP and NEE were then summed to give annual fluxes as g CO_2 m^{-2} yr^{-1}.

$$NEE = -(GPP - R_{eco}) \quad \text{Eq. 22}$$

where NEE is net ecosystem exchange (mg CO_2 m^{-2} h^{-1}), GPP is gross primary production (mg CO_2 m^{-2} h^{-1}) and R_{eco} is ecosystem respiration (mg CO_2 m^{-2} h^{-1}).

6.2.1.2 CH_4 emission modelling

Annual terrestrial CH_4 fluxes were also reconstructed using regression analysis to infill CH_4 emissions. As for annual CO_2 fluxes, spatial variation in plant community was incorporated into the model as to improve model performance (Kettunen et al., 2000, Laine et al., 2007b, Laine et al., 2009), resulting in mixed-effects models being used due to the lack of sufficient data arising from issues with ebullition (section 6.2.1) to parameterise individual collar models. All data for both sites and all collars were therefore

included in the regression analysis. Unlike CO_2 infill modelling, an additive linear mixed-effects model was used as independent variables could be normalised and standardised. An additive approach was used on independent variables based on process knowledge, as there is a lack of theoretical and empirical basis to use a multiplicative approach, such as in the case for GPP and R_{eco} (section 6.2.1.1).

Firstly, the dependent variable was normalised. Independent variables were then checked to see if they were correlated with each other in order to eliminate collinearity. Any variables that were significantly correlated with each other, the variable that had the weakest correlation with the dependent variable was removed from the variable list (Table 38). Furthermore, any variable that was not correlated with CH_4 flux was removed from the variable list, unless a clear ecological reason for leaving the parameter in exists, e.g. the effect of temperature on methanogenesis. A shortlist of candidate variables was created (Table 40) with data logged at an hourly interval as to facilitate infill modelling at an hourly interval. Independent variables were then normalised and standardised to give values between 0 and 1 using Eq. 18 (section 4.2.7). Dependent and independent variables were then checked for normality using qqnorm plots and transformed.

Table 40 Final independent variables for CH_4 infill modelling.

Independent variable
Peat temperature (PT)
Water level (WL)
VGA
Barometric pressure (Baro)
Wind speed
Relative humidity

Hourly estimates for CH_4 emissions were then summed to give annual fluxes as g CH_4 m^{-2} yr^{-1}.

6.2.2 CO_2-equivalent conversion

In order to compare CO_2 and CH_4 at each site (R.Q.6), CH_4 was converted into CO_2-equivalents using the global warming potential (GWP) over a 20-, 100- and 500-year

horizon (Drewer et al., 2010, Grossmann and Dietrich, 2012). The different time periods do not indicate any effect of climate change, more the potential for CH_4 to warm the atmosphere over different time periods on a molecule-per-molecule basis in comparison to CO_2, taking into account the removal by OH radicals in the stratosphere. Annual CH_4 fluxes were multiplied by 62, 25 or 7 to convert into CO_2-equivalents over 20-, 100- and 500-year horizons (Drewer et al., 2010).

6.2.3 Relative importance of aquatic and terrestrial CH_4 emissions

Observed CH_4 emissions reported in section 4.3 showed ditch fluxes to be significantly greater than fen fluxes. To ascertain if ditches emitted more CH_4 than the fen, the relative importance of fluxes by surface area were calculated by scaling annual CH_4 fluxes by the surface area of the fen and ditches. An annual ditch flux was calculated using the same methodology in section 6.2.2. The geometry of the fen and intersecting ditches were calculated using shape files from MaterMaps (OS MasterMapTopography Layer [GML geospatial data], 2014b, OS MasterMapTopography Layer [GML geospatial data], 2014a) in ArcGIS (version 9.3). Annual fluxes were spatially extrapolated using the following equation (Eq. 23) from Schimel and Potter (1995):

$$F = \sum(A_i \cdot F_i) \qquad \text{Eq. 23}$$

where F is the total scaled annual ditch or fen flux (Mg CH_4 yr^{-1}), A_i is the area of the ditch or fen (km^2) and F_i is the area-specific annual flux (Mg CH_4 km^{-2} yr^{-1}). The method does not take ecological differences external to the defined area (section 3.1.3) into account (Becker et al., 2008). However, it is the simplest and most commonly used method (Schimel and Potter, 1995) and was thus chosen to quantify the relative importance of aquatic and terrestrial fluxes.

6.2.4 Statistical analysis.

All statistical work was undertaken in R version 3.1.1 (R Core Team, 2014). Independent variables for infill modelling were examined for correlations with the dependent variable using Spearman's rank correlations, undertaken using rcorr function in the Hmisc package (Harrell and Dupont, 2015). Linear and non-linear mixed effects models for VGA, GPP, R_{eco} and CH_4 infill modelling using lme4 (Bates et al., 2014) and nlme (Pinheiro et al., 2014). AICc was used to compare models and the aictab function to find the best fitting model using AICcmodavg package (Mazerolle, 2013). Model efficiency (MEF; section 6.2.1) was calculated using NSE function in hydroGOF package (Zambrano-Bigiarini, 2014). Data was checked for normality using qqnorm plots (R Core

Team, 2014) and transformed using Box-cox transformations in the MASS package (Ripley et al., 2002). A linear mixed-effects model was used to establish differences in water level between sites using the lme function in nlme (Pinheiro et al., 2014). Independent t-tests were used to investigate differences in annual R_{eco}, GPP, NEE and CH_4 fluxes between sites (H_8). Independent t-tests were also used to compare CO_2-equivalent fluxes for CO_2 and CH_4 (H_9), to establish which gas had greater emissions at both sites, and to compare total C exchange between sites (H_{10}). Independent t-tests were undertaken using the stats package (R Core Team, 2014).

6.3 Annual terrestrial C exchange

6.3.1 Annual fen CO_2 exchange

Daily VGA was modelled in order to model annual fen CO_2 exchange. Coefficients for the best fitting VGA model are in Table 41 and the mean response for both sites is shown within Figure 68 for both 2012 and 2013 (individual collar responses are shown in Figure 69 and 70 for Sutton and Strumpshaw Fen, respectively). Some bias in the VGA models may exist (MEF = 0.71) due the best phenology model not fully capturing the variation between collars (Figure 71B, SuC3 and StC3), only variation between the two sites; however, the phenology model was the best fitting model based on AICc comparisons between different models and from observing residual plots (Figure 71A). A model separating out the two growing years was tried but resulted in a poorer AICc value and a pattern in the residuals. Thus, this model was rejected.

Table 41 Summary statistics for the VGA infill model created using mixed-effects non-linear least square regression, where $Daily\ VGA$ ($m^2\ m^{-2}$) is the response variable; $julian$ is the independent variable (no site fixed effect); VGA_{max} ($m^2\ m^{-2}$), x_{max} and b are fitted parameters; and random variation between collars for fitted parameters.

Equation: $Daily\ VGA = VGA_{max} \cdot e^{(-0.5\left(\frac{julian - x_{max}}{b}\right)^2)}$					
Formula: = VGA_{max} + x_{max} + b~1|collar					
Sutton	VGA_{max}	x_{max}	b		
1	3.1	231	53		
2	3.4	232	54		
3	5.1	236	55		
4	4.0	233	54		
5	3.6	232	54		
6	5.4	237	56		
Strumpshaw					
1	8.2	226	55		
2	6.8	223	54		
3	8.7	228	56		
4	6.1	221	53		
5	6.2	221	53		
6	7.0	223	54		
Fixed effects: $Daily\ VGA = VGA_{max} \cdot e^{(-0.5\left(\frac{julian - x_{max}}{b}\right)^2)}$					
	Value	Std. error	DF	*t-value*	*p*-test
VGA_{max}	5.6	1.1	142	4.9	< 0.001
x_{max}	229	4.9	142	46	< 0.001
b	54	3.2	142	17	< 0.001

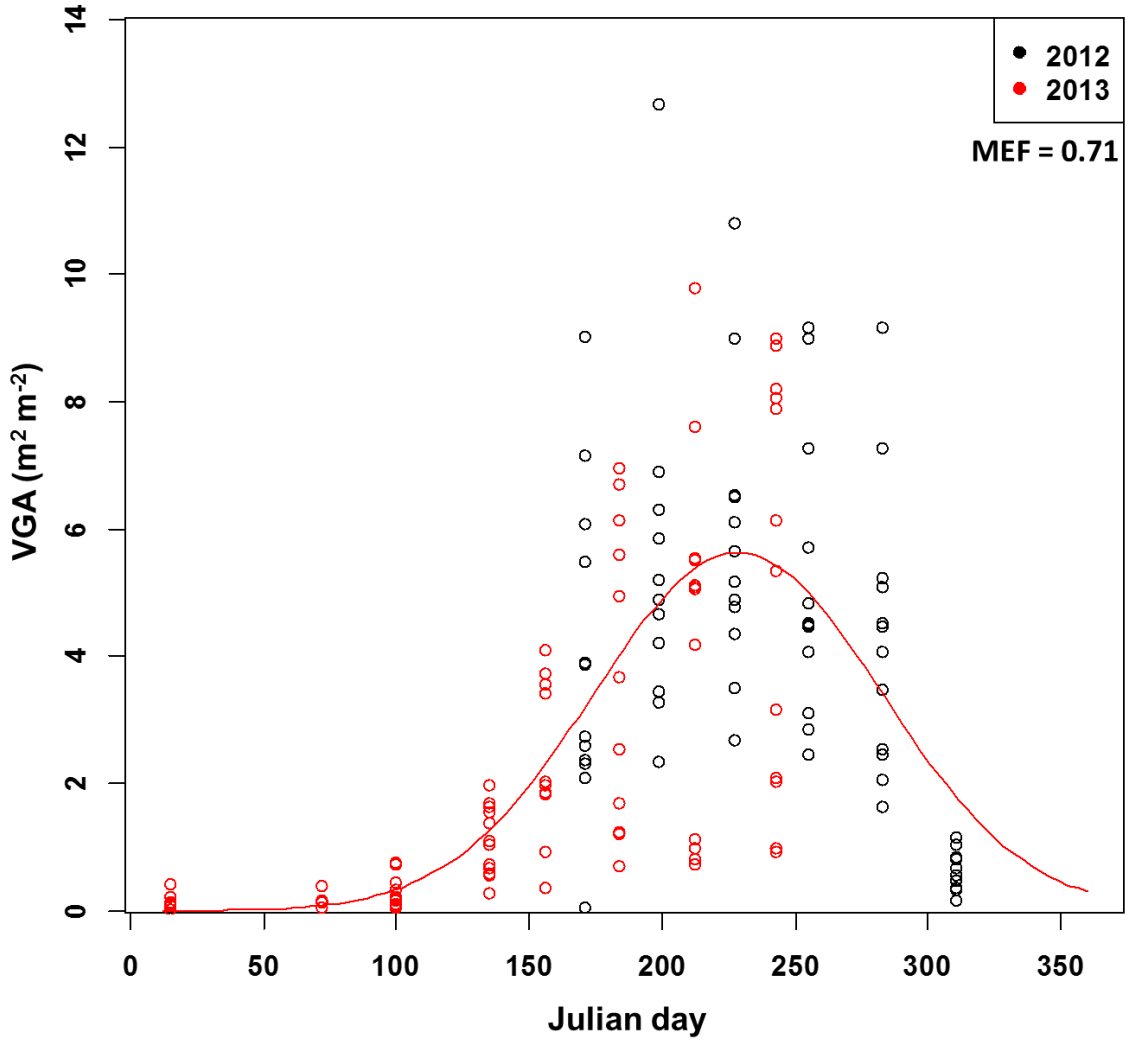


Figure 68 VGA response for all collars at Sutton and Strumpshaw from June 2012 to September 2013 and the mean response from the mixed-effects phenology model.

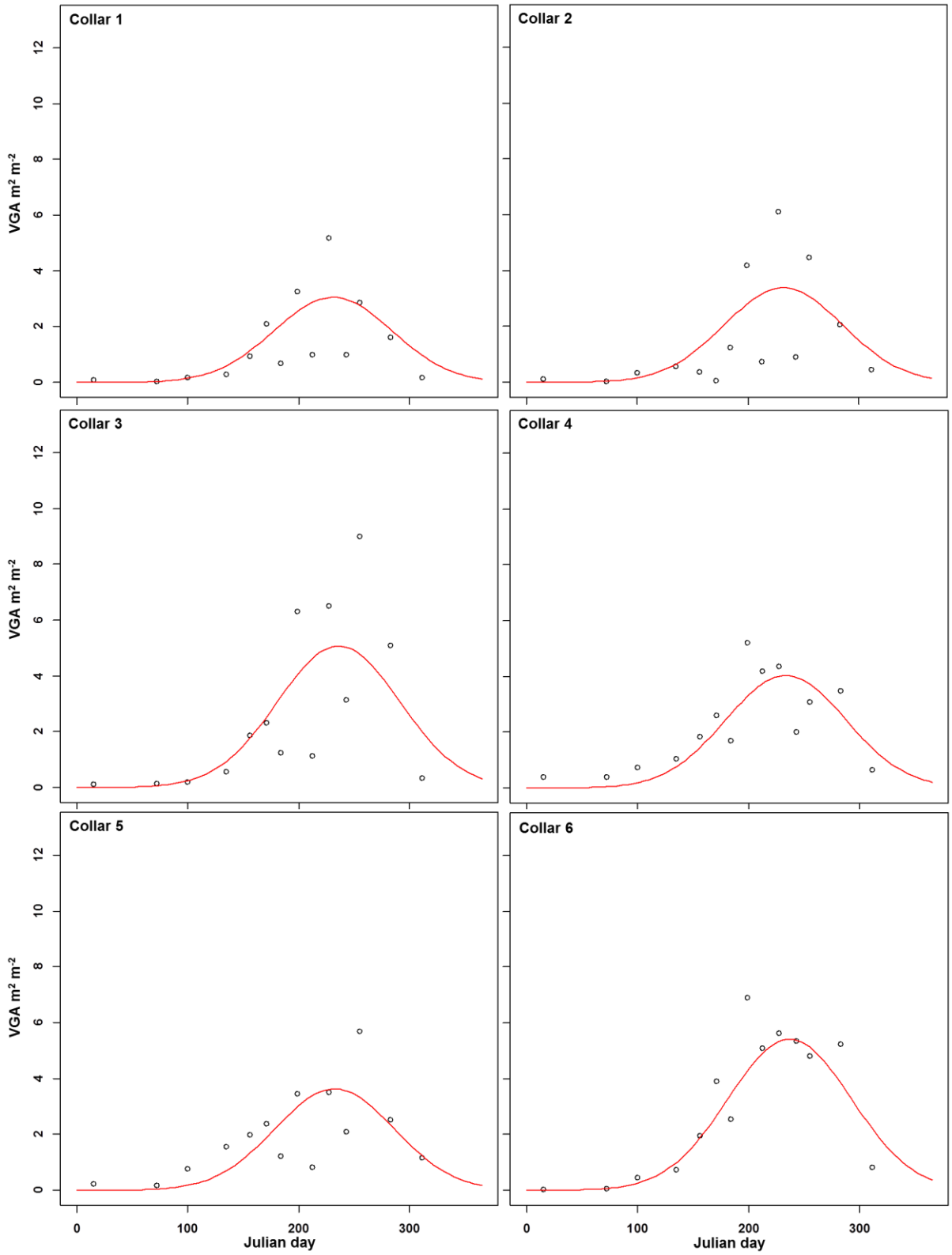


Figure 69 Individual collar VGA at Sutton Fen over both 2012 and 2013 and the mixed-effects phenology model response (red line) for each collar.

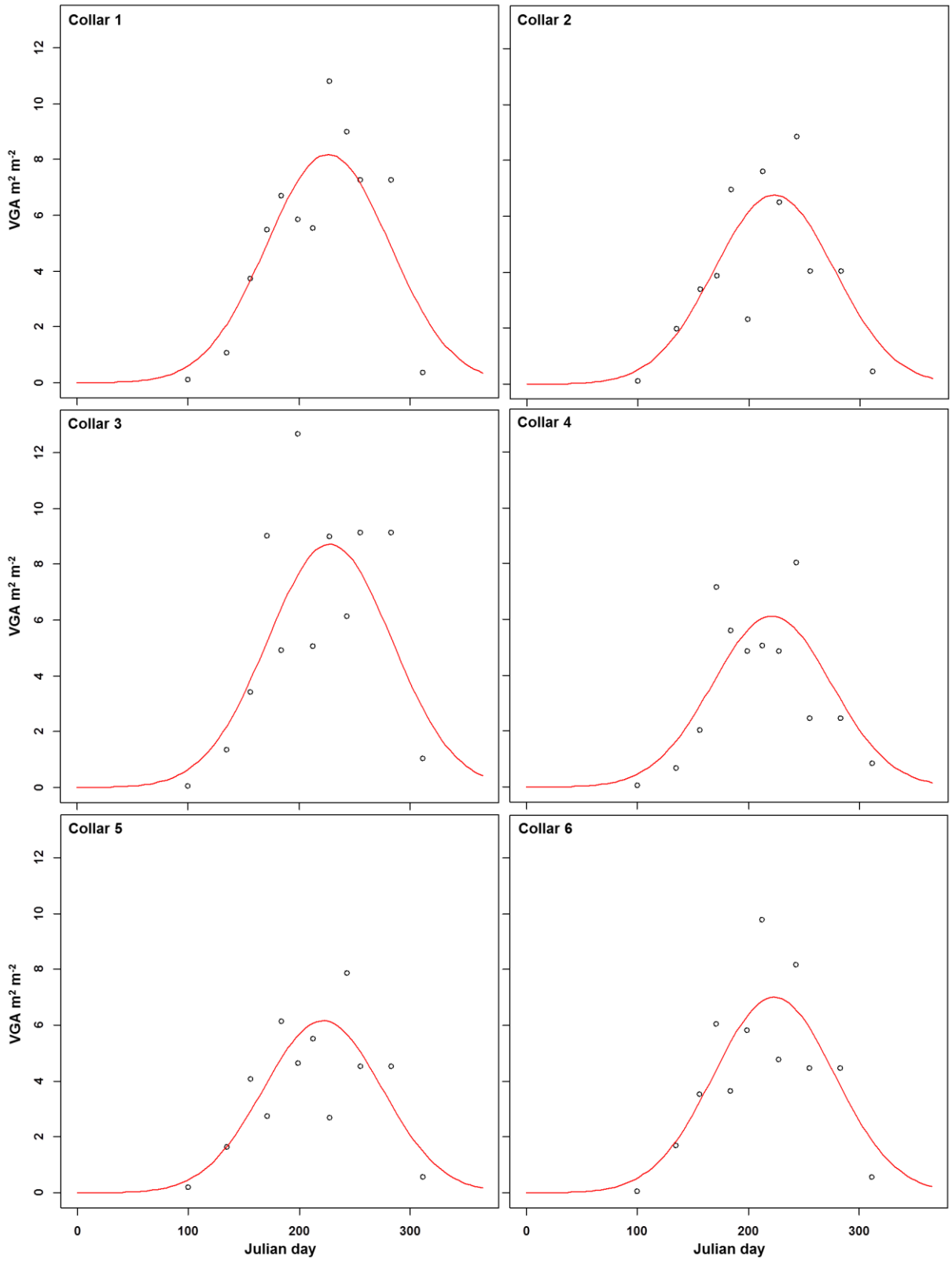


Figure 70 Individual collar VGA at Strumpshaw Fen over both 2012 and 2013 and the mixed-effects phenology model response (red line) for each collar.

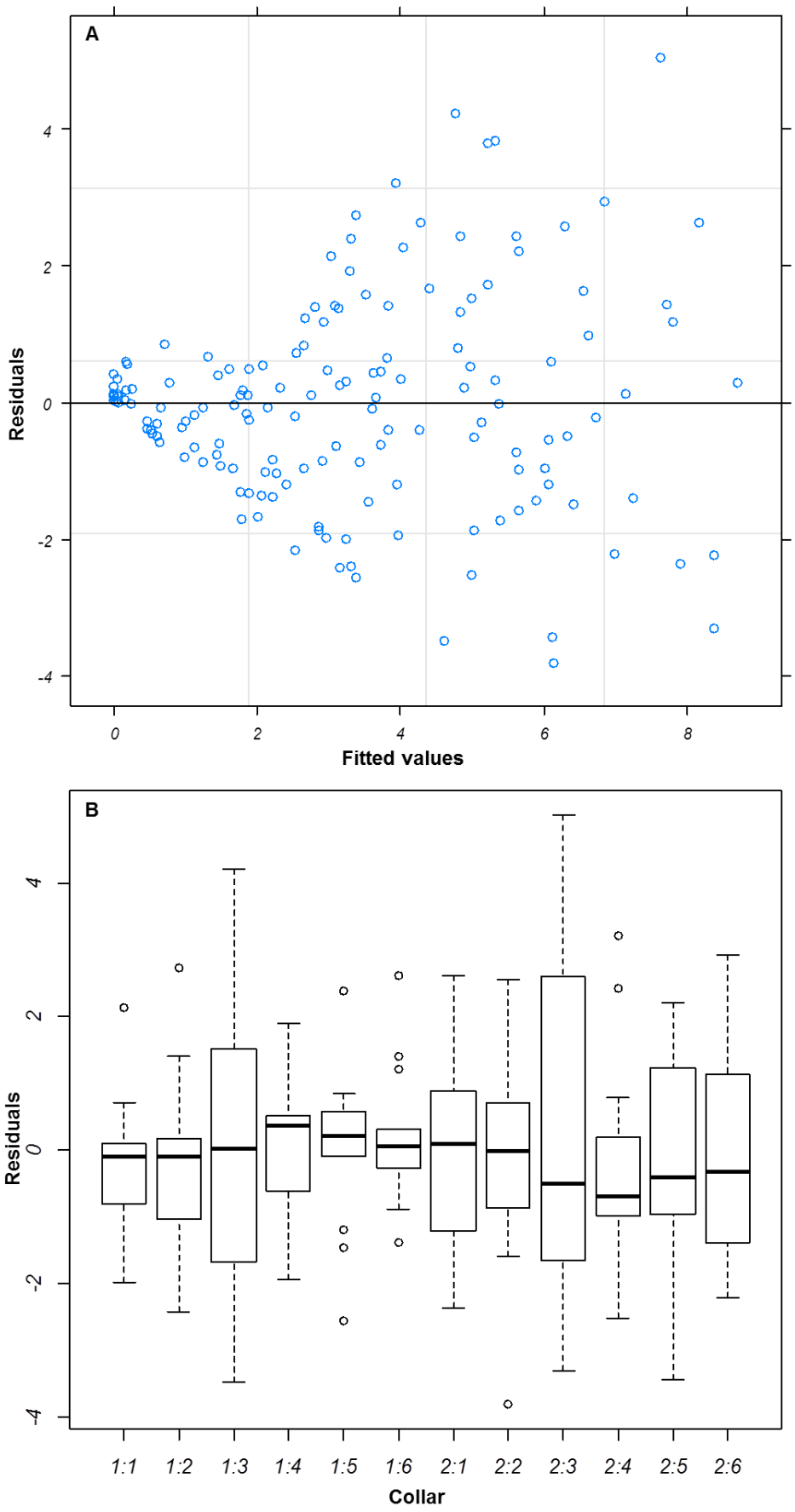


Figure 71 Validation plot (A) of residuals vs fitted VGA values ($m^2\ m^{-2}$) and (B) collar specific residuals (1: = Sutton, 2: = Strumpshaw).

Correlation coefficients for independent variables and R_{eco} and GPP are shown in Table 29 and 30, respectively, in section 4.3.6. The only independent variable to be included that was not significantly correlated with the dependent variable is PAR in the GPP model (Table 30). PAR was included as it is a measure of infrared radiation that is used by vegetation to photosynthesis and is therefore necessary for GPP. Table 42 and Table 43 show ΔAICc for R_{eco} and GPP model selection, respectively. Table 44 reports coefficients for the best R_{eco} model (MEF = 0.66), which did not have site as a fixed effect but included collar as a random effect on water level. The model had VGA, peat temperature at 5 cm and water level as independent variables. R_x, a basal respiration rate at 0 °C as in Kandel et al. (2013a); and b1, b2 and b3 as scaling factors for VGA, peat temperature and water level, respectively, as fitted parameters. The standardised within group residuals were normally distributed (Figure 72) and there was no substantial deviations in residuals seen in the collars or site (Figure 73C and 73D, respectively). The best GPP model (MEF = 0.69), on the other hand, had site as a random effect on pmax (fitted parameter; Table 45). GPP had PAR, VGA, air temperature and water level as independent variables. Fitted parameters included pmax, kabs, ktemp, kwl and kpar. Pmax was a parameter describing light use efficiency – the ratio of C biomass production per unit of absorbed light – as outlined in Kiene and Hines (1995). Kabs was a vegetation extinction coefficient, whilst ktemp and kwl were scaling factors, as in Kiene and Hines (1995). The standardised within group residuals were normally distributed (Figure 74) and there was no substantial deviations from homogeneity seen in the data (Figure 75).

Table 42 Model selection and comparison using ΔAICc, AICc, -loglik and AICcweight for R_{eco} (response variable). Predictor variables include VGA, peat temperature at 5 cm (PT) and water level (WL). Site (1|Site) or collar (1|Collar) were included as a random effect on selected parameters.

Model	Random effect	-loglik	-loglik df	AICc	ΔAICc	AICc w_i
(Rx+b1*VGA)*exp(b2*PT)*exp(b3*WL)	b3|Collar	1042	6	2095	0.00	0.57
(Rx+b1*VGA)*exp(b2*((1/(Tref-T0))-(1/(PT-T0))))	b1+b2|Collar	1043	9	2096	1.23	0.31
(Rx+b1*VGA)*exp(b2*PT)*exp(b3*WL)	b1+b2+b3|Collar	1045	16	2099	3.92	0.08
(Rx+b1*VGA)*exp(b2*PT)*exp(b3*WL)	B3|Site	1046	5	2101	5.49	0.04
(Rx+b1*VGA)*exp(b2*((1/(Tref-T0))-(1/(PT-T0))))	b1+b2|Site	1050	6	2109	14.25	0.00

Table 43 Model selection and comparison using ΔAICc, AICc, -loglik and AICcweight for GPP (response variable). Predictor variables include VGA, air temperature (AT) and water level (WL). Pmax, kabs, ktemp, kwl and kpar are fitted parameters. Site (1|Site) or collar (1|Collar) were included as a random effect on selected parameters.

Model	Random effect	-loglik	-loglik df	AICc	ΔAICc	AICc w_i
pmax*(par/(kpar+par))* VGA ^(kabs*exp(ktemp* AT)*exp(kwl* WL))	pmax|Collar	1028	8	2073	0.00	0.59
pmax* VGA ^(kabs*exp(ktemp* AT)*exp(kwl* WL))	pmax|Site	1031	6	2075	2.46	0.17
pmax*(par/(kpar+par))* VGA ^(kabs*exp(ktemp* AT)*exp(kwl* WL))	pmax|Site	1031	7	2076	3.91	0.08
pmax*exp(ktemp* AT)* VGA*kabs*exp(kwl*WL)	Pmax+kabs+kwl|Site	1026	11	2077	4.57	0.06
pmax* exp(ktemp* AT)*VGA^kabs	ktemp|Site	1035	5	2080	7.84	0.01
pmax*(par/(kpar+par))* VGA ^(kabs*exp(ktemp* AT)*exp(kwl* WL))	pmax+kpar|Collar	1028	12	2082	9.53	0.01

Table 44 Summary statistics for the model created using mixed-effects non-linear least square regression, where R_{eco} (mg CO_2 m^{-2} h^{-1}) is the response variable; ecosystem respiration at 0 °C (Rx; mg CO_2 m^{-2} h^{-1}), VGA (m^2 m^{-2}), peat temperature at 5 cm (PT; ˚C) and water level (WL; cm above peat surface) are the independent variable (no site fixed effect) and the model has the same slope for both sites but with random variation (intercept) between collars.

Equation: $R_{eco} = (\mathrm{Rx} + \mathrm{b1} \cdot \mathrm{VGA}) \cdot \exp(\mathrm{b2} \cdot \mathrm{PT}) \cdot \exp(\mathrm{b3} \cdot \mathrm{WL})$					
Random effects:	-loglik$_6$ = 1042				
Formula: = b3~1|collar	Intercept	Residual			
Std. Dev.	0.00003	488.62			
Sutton	Intercept		Strumpshaw	Intercept	
1	0.0037		1	-0.054	
2	0.0020		2	-0.44	
3	-0.020		3	-0.067	
4	-0.0056		4	-0.28	
5	0.00088		5	-0.056	
6	0.0012		6	-0.027	
Fixed effects: R_{eco} = (Rx+b1*VGA)*exp(b2*PT)*exp(b3*WL)					
	Value	Std. error	DF	*t-value*	*p*-value
b1	0.96	1.8	123	0.53	0.60
b2	0.15	0.011	123	14	< 0.001
b3	-0.024	0.017	123	-1.4	0.16

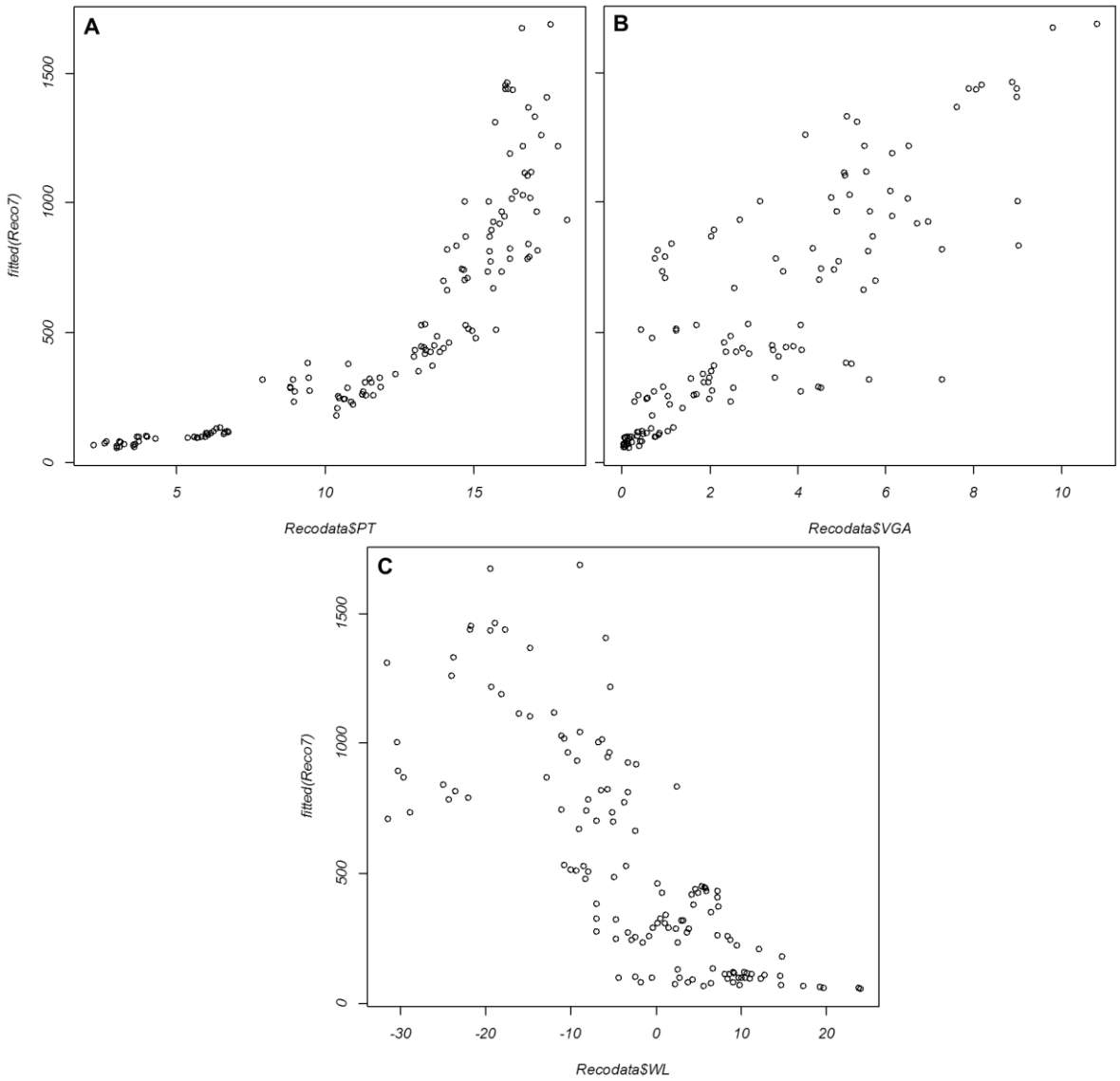


Figure 72 Scatter plot of fitted R_{eco} (mg CO_2 m^{-2} h^{-1}) and (A) peat temperature at 5 cm below surface (PT; ˚C), (B) VGA (m^2 m^{-2}) and (C) water level (WL; cm above peat surface).

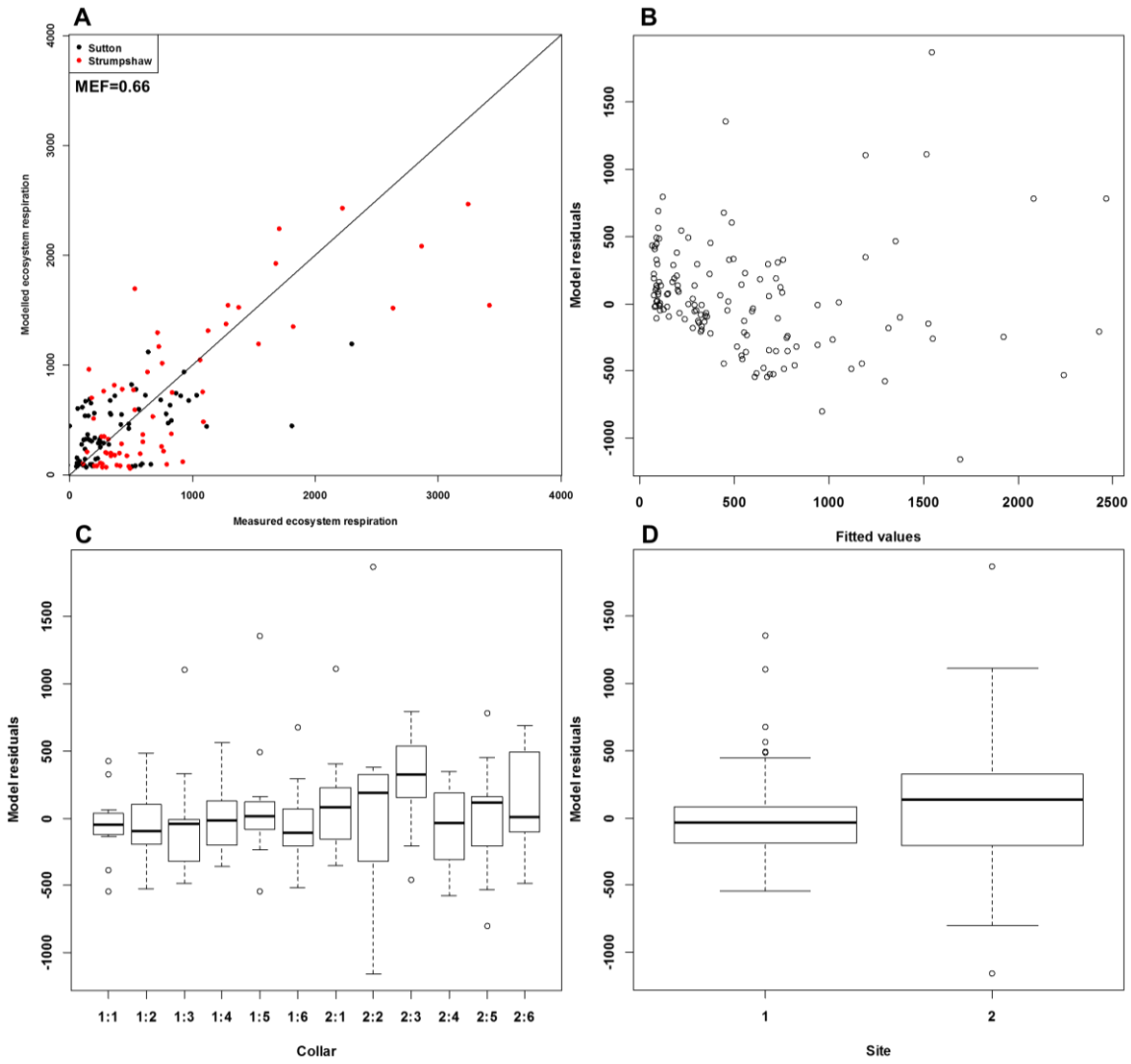


Figure 73 Validation plot (A) of observed vs fitted R_{eco} values (mg CO_2 m^{-2} h^{-1}) with a 1:1 line and (b) residuals vs. fitted R_{eco} values (mg CO_2 m^{-2} h^{-1}) to test the assumptions of homogeneity. Plot (C) shows residuals per collar (1: = Sutton, 2: = Strumpshaw) from the optimal model and plot (D) shows residuals per site (1 = Sutton, 2 = Strumpshaw).

Table 45 Summary statistics for the model created using mixed-effects non-linear least square regression, where GPP (mg CO_2 m^{-2} h^{-1}) is the response variable; PAR (µmol m^{-2} s^{-1}), VGA (m^2 m^{-2}), air temperature (AT; ˚C) and water level (WL; cm above peat surface) are the independent variable (no site fixed effect) and random variation between collar for pmax (mg CO_2 m^{-2} h^{-1}). Kpar (µmol m^{-2} s^{-1}), kabs, ktemp and kwl are fitted parameters.

Equation: $GPP = pmax \cdot (\frac{par}{kpar+par}) \cdot VGA^{(kabs \cdot \exp(ktemp \cdot AT) \cdot \exp(kwl \cdot WL))}$					
		-loglik$_8$ = 1080			
Random effects:					
Formula: = pmax + (1|Collar)					
	Intercept	Residual			
Std. Dev.	140	554			
Sutton	Intercept		Strumpshaw		
1	981		1		1084
2	894		2		833
3	767		3		980
4	806		4		795
5	843		5		750
6	926		6		853
	Value	Std. error	DF	t-value	*p*-value
pmax	876	132	123	6.6	< 0.001
kpar	47	36	123	1.3	0.20
ktemp	0.01	0.03	123	0.41	0.68
kabs	0.26	0.12	123	2.2	0.027
kwl	0.003	0.01	123	0.21	0.83

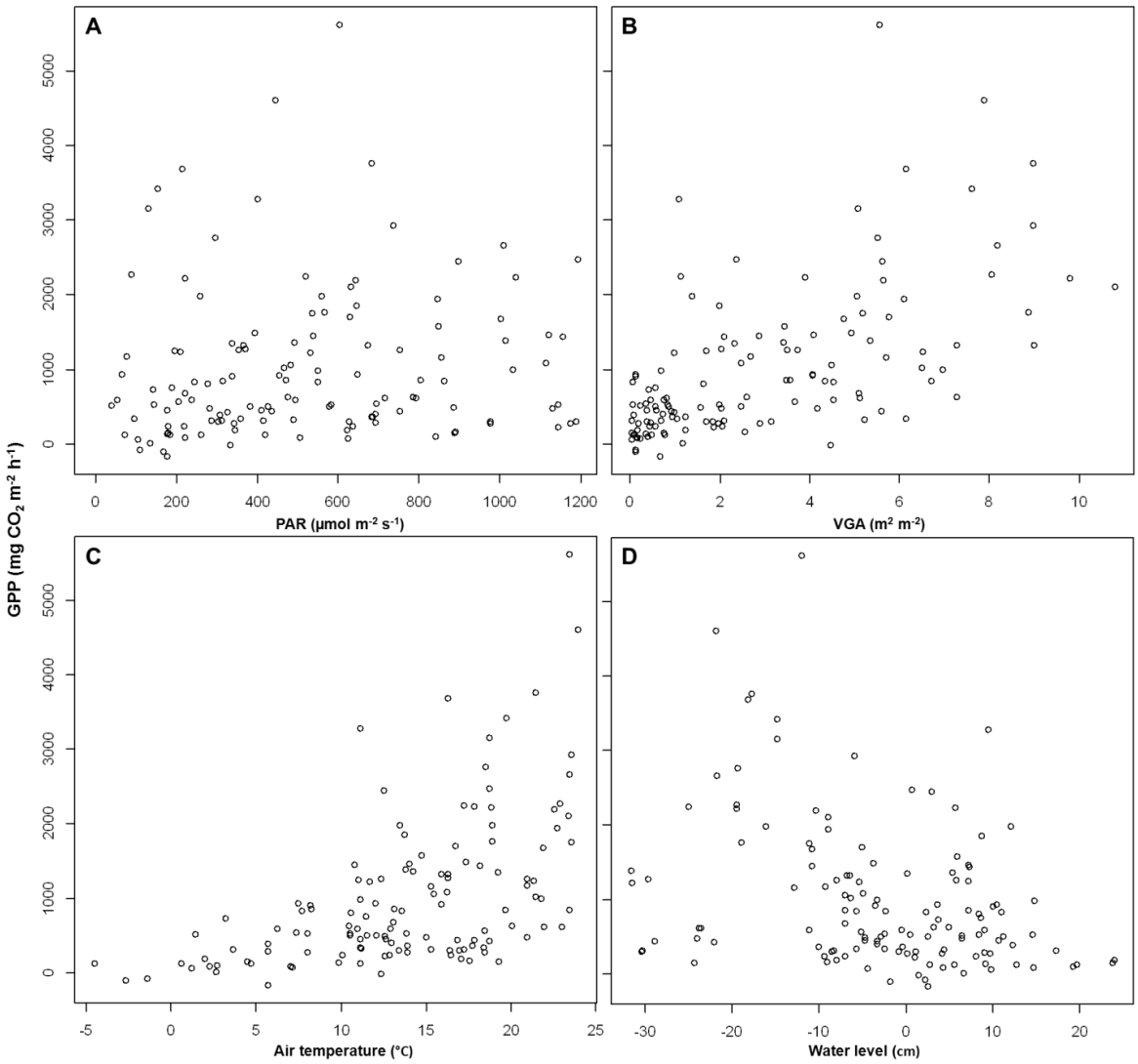


Figure 74 Scatter plot of GPP and (A) PAR, (B) VGA, (C) air temperature and (D) water level.

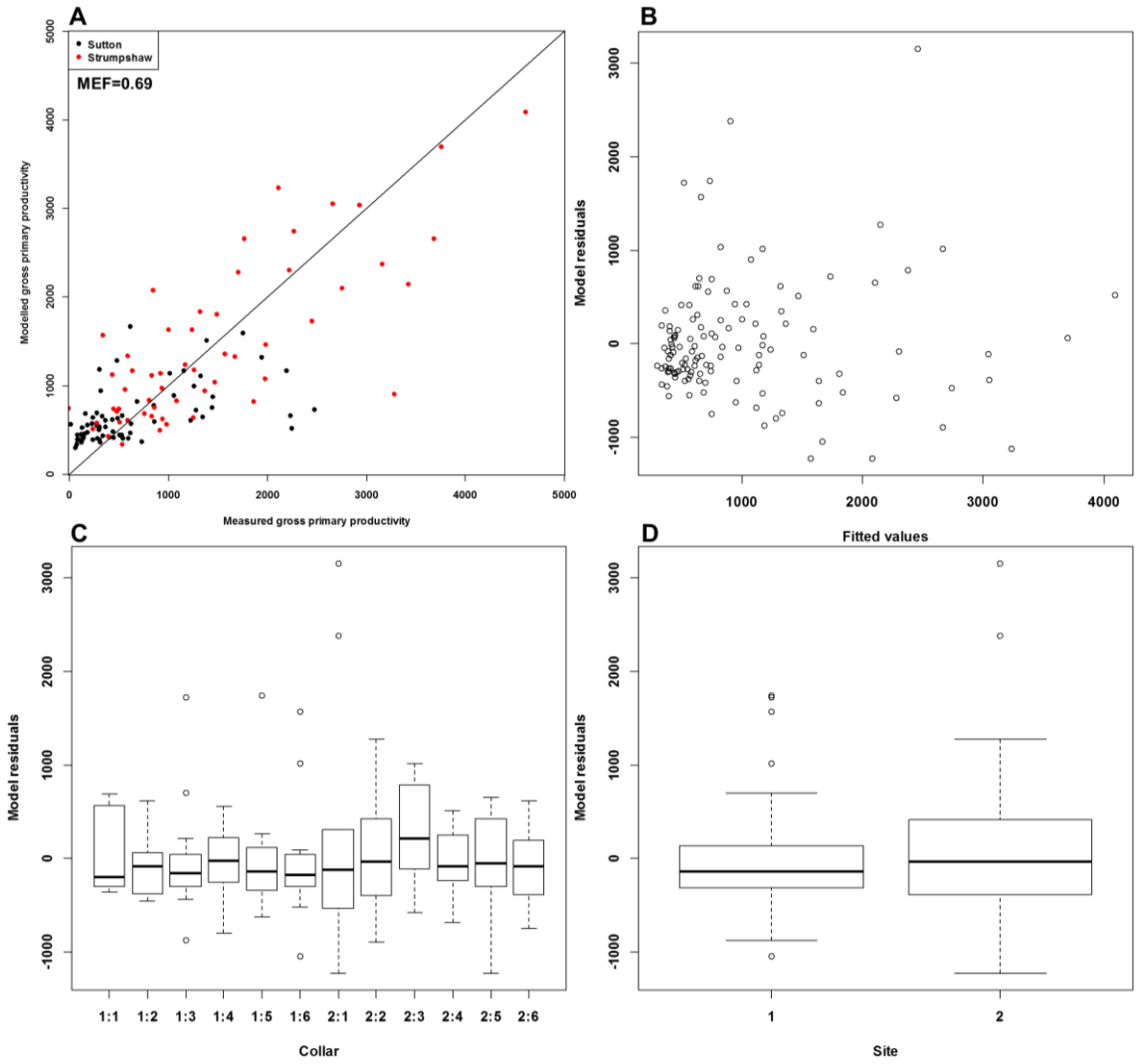


Figure 75 Validation plot (A) of observed vs fitted GPP values (mg CO_2 m^{-2} h^{-1}) with a 1:1 line and (b) residuals vs. fitted GPP values (mg CO_2 m^{-2} h^{-1}). Plot (C) shows residuals per collar (1: = Sutton, 2: = Strumpshaw) from the optimal model and plot (D) shows residuals per site (1 = Sutton, 2 = Strumpshaw).

Hourly R_{eco} estimates were reconstructed for each collar using the model in Table 44. The model in Table 45 was used to estimate hourly GPP. Hourly NEE was then estimated by subtracting R_{eco} from GPP estimates for each collar (Chapin et al., 2006). Annual R_{eco}, GPP and NEE were calculated by summing the hourly estimates for the year. The average annual fluxes varied between collars (Table 46, 47 and 48 for R_{eco}, GPP and NEE, respectively). Average annual reconstructed R_{eco} was 2725 ± 103 g CO_2 m^{-2} yr^{-1} at Sutton Fen and 3479 ± 154 g CO_2 m^{-2} yr^{-1} at Strumpshaw Fen. R_{eco} was significantly different between sites ($t_{8.928}$ = -4.0607, p = 0.003) and there was little variation in emission between collars (Table 46). R_{eco} estimates may be slightly biased as the reconstruction model underestimated larger summer fluxes (Figure 73A); however, low-

and mid-range fluxes were generally well estimated. GPP was significantly greater at Strumpshaw Fen than at Sutton Fen ($t_{5.33}$ = -3.8835, p = 0.01; 2814 ± 103 and 5039 ± 564 g CO_2 m^{-2} yr^{-1} for Sutton and Strumpshaw, respectively). The GPP predicted versus observed fluxes (Figure 75A) centred around the 1:1 line, with some of the higher summer month CO_2 uptake were underestimated by the model. It is anticipated, however, that this is only for extremely high CO_2 uptake as observed in summer 2013 (Figure 42). There was some variation within residuals between collars (Figure 75C). The difference in GPP and R_{eco} translated into a greater range in reconstructed NEE at Strumpshaw Fen (-3138 to -652 g CO_2 m^{-2} yr^{-1}) than at Sutton Fen (-509 to 374 g CO_2 m^{-2} yr^{-1}). NEE was also significantly different between sites ($t_{6.094}$ = 3.3393, p = 0.015); Sutton Fen was a smaller sink of CO_2 (average of all collars; -90 ± 139 g CO_2 m^{-2} yr^{-1}; Table 31) than Strumpshaw Fen (-1560 ± 418 g CO_2 m^{-2} yr^{-1}) between 1st September 2012 and 31st August 2013. Greatest CO_2 emissions and uptake were observed in the summer periods at both sites. Reconstructed NEE results (Figure 76 and 77) were generally reasonably estimated.

Model sensitivity analysis was performed on the reconstructed annual flux by varying parameters by ± 10% (Figure 78 and 79). R_{eco} was sensitive to peat temperature, with alterations by ± 10 % causing a change in flux > 10 % but < 20 % than the original modelled R_{eco} estimate. R_{eco} was less sensitive to alterations in VGA and water level (< 5 % change in CO_2 emission from the original flux). GPP was not as sensitive to any of the parameters (< ± 5 % variance from the original modelled R_{eco} estimate).

Table 46 Reconstructed R_{eco} statistics for each collar from 1st September 2012 to 31st August 2013.

Site	Collar	Annual R_{eco} (g CO_2 m^{-2} yr^{-1})	Hourly R_{eco} (mg CO_2 m^{-2} h^{-1})			
			Mean	Standard error	Minimum	Maximum
Sutton	1	2540	290	2.1	75	829
	2	2579	294	2.2	74	866
	3	3217	367	4.0	51	1536
	4	2759	315	2.7	69	1045
	5	2606	298	2.3	73	892
	6	2646	302	2.3	74	908
Strumpshaw	1	3663	418	6.1	4.3	2432
	2	3663	384	5.1	7.9	2016
	3	4066	646	7.5	2.0	3009
	4	3074	351	4.0	20	1545
	5	3606	412	6.1	4.0	2415
	6	3100	354	4.1	21	1554

Table 47 Reconstructed GPP statistics for each collar from 1st September 2012 to 31st August 2013.

Site	Collar	Annual GPP (g CO_2 m^{-2} yr^{-1})	Hourly GPP (mg CO_2 m^{-2} h^{-1})			
			Mean	Standard error	Minimum	Maximum
Sutton	1	3049	348	4.5	0	1953
	2	2644	302	4.0	0	1804
	3	2978	340	4.9	0	2605
	4	2386	272	3.7	0	1811
	5	2928	334	4.5	0	2081
	6	2900	331	4.9	0	2640
Strumpshaw	1	6160	703	9.0	0	4494
	2	4599	525	6.6	0	3076
	3	7204	822	11	0	5404
	4	3748	428	5.3	0	2400
	5	4771	545	6.7	0	3063
	6	3752	428	5.4	0	2552

Table 48 Reconstructed NEE statistics for each collar from 1st September 2012 to 31st August 2013.

Site	Collar	Annual NEE (g CO_2 m^{-2} yr^{-1})	Hourly NEE (mg CO_2 m^{-2} h^{-1})			
			Mean	Standard error	Minimum	Maximum
Sutton	1	-509	-58	3.9	-1429	829
	2	-65	-7.5	3.4	-1251	866
	3	239	27	4.2	-1531	1536
	4	374	43	3.2	-1113	1045
	5	-321	-37	3.8	-1508	892
	6	-255	-29	4.1	-2053	908
Strumpshaw	1	-2497	-285	7.7	-2768	2432
	2	-1236	-141	5.8	-1672	2016
	3	-3138	-358	9.1	-3225	3009
	4	-674	-77	4.6	-1343	1545
	5	-1165	-133	6.3	-1344	2415
	6	-652	-75	4.7	-1496	1554

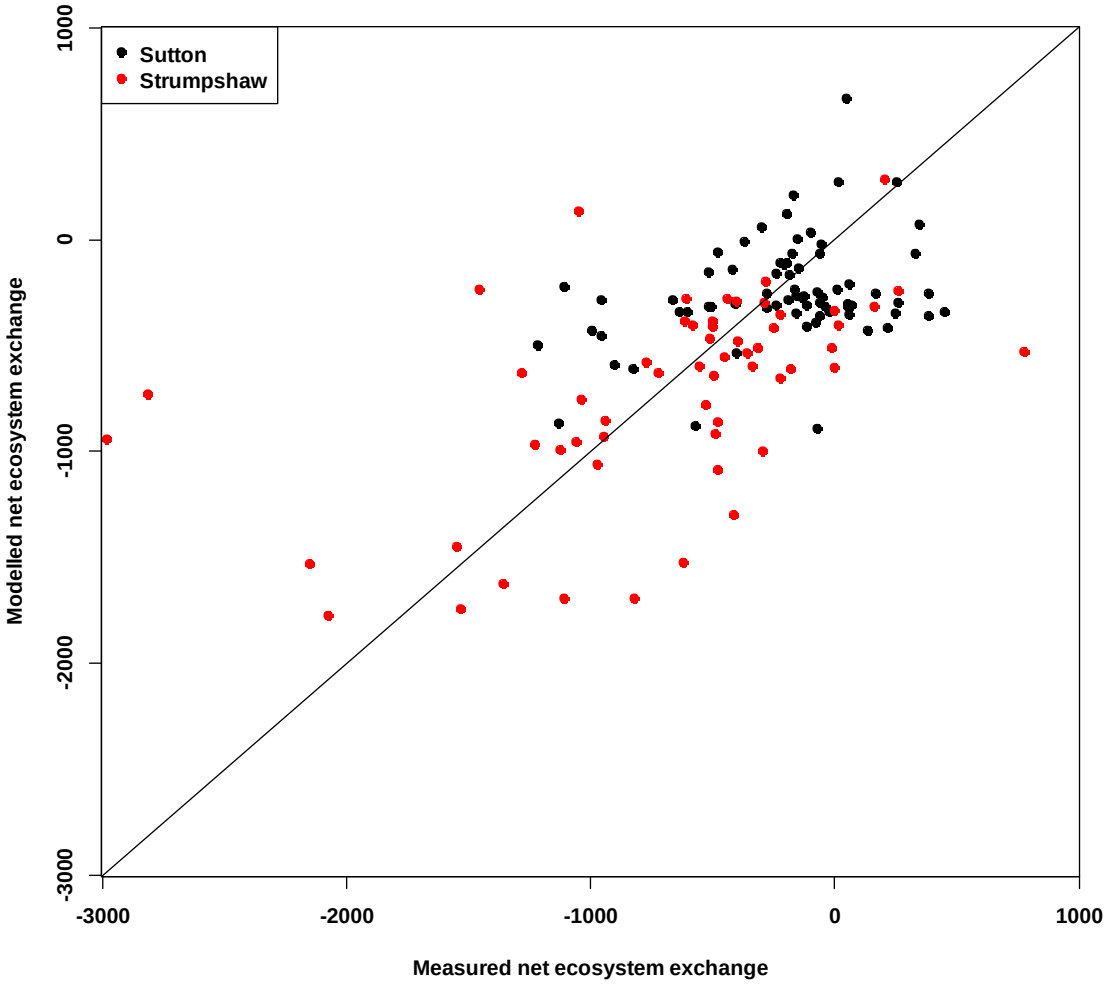


Figure 76 Validation plot of observed vs fitted NEE values (mg CO_2 m^{-2} h^{-1}) with a 1:1 line for Sutton and Strumpshaw Fen.

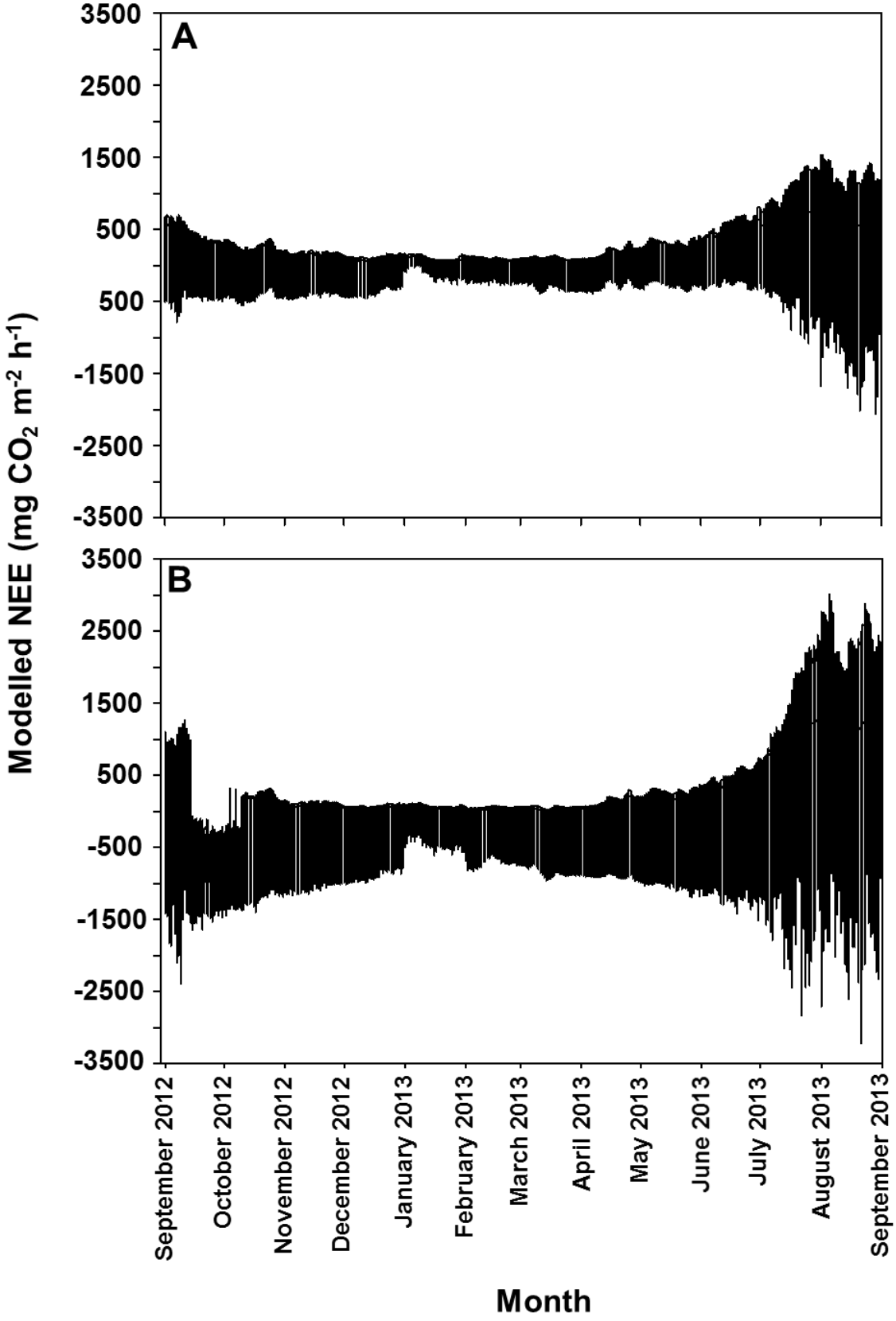


Figure 77 Mean (all collars) hourly reconstructed NEE (negative indicates CO_2 uptake) for Sutton (A) and Strumpshaw Fen (B).

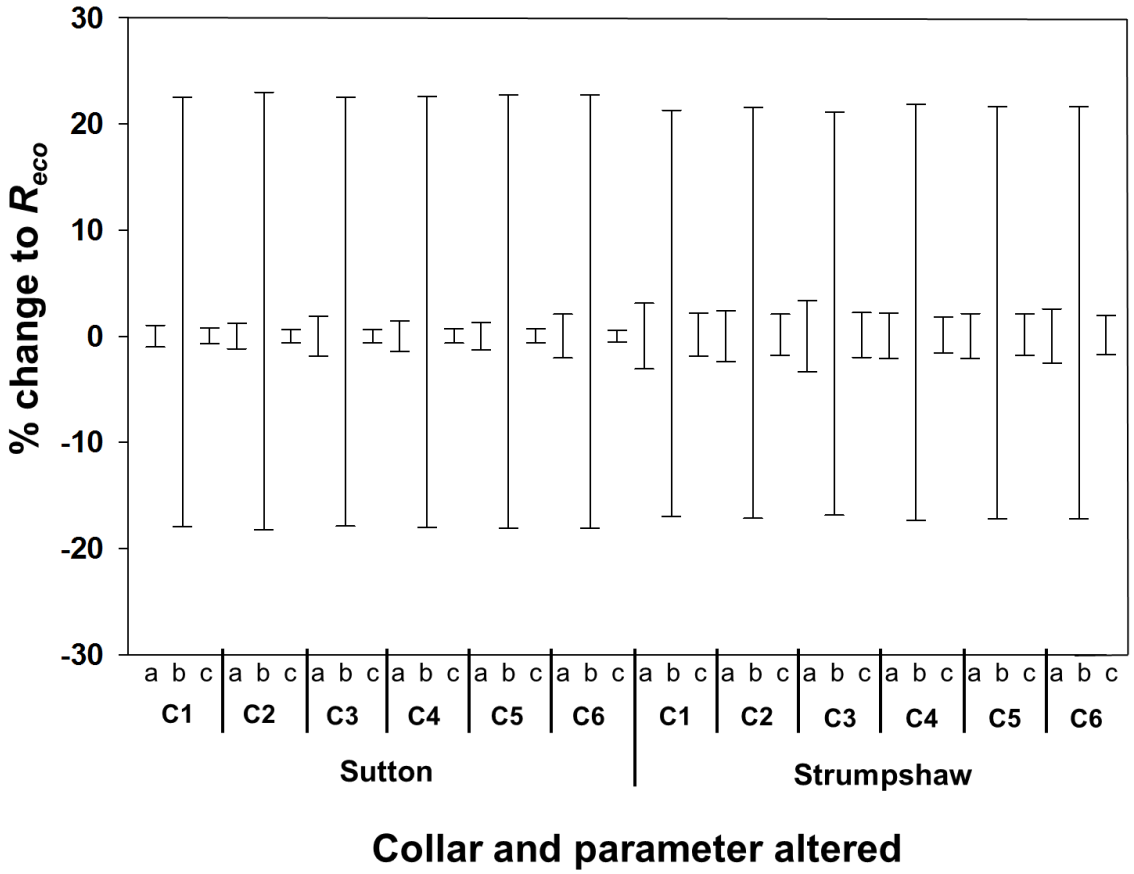


Figure 78 Sensitivity analyses of % change in annual R_{eco} (g CO_2 m^{-2} yr^{-1}) to alterations by ± 10 % to parameters (VGA (a; m^2 m^{-2}) peat temperature (b; ˚C) and water level (c; cm above peat surface)) for each collar at Sutton and Strumpshaw Fens.

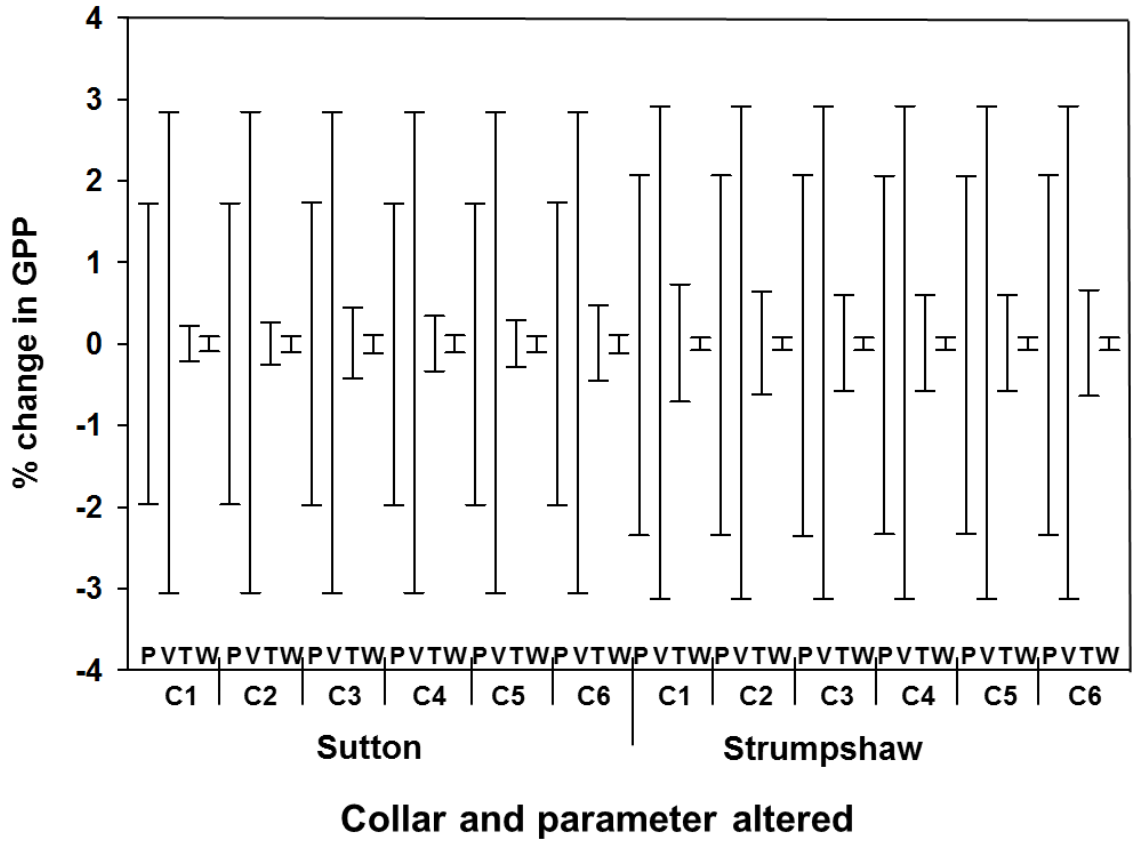


Figure 79 Sensitivity analyses of parameters (PAR (P; µmol m^{-2} s^{-1}), VGA (V; m^2 m^{-2}) air temperature (T; ˚C) and water level (W; cm above peat surface)) in relation to annual GPP (g CO_2 m^{-2} yr^{-1}) for each collar at Sutton and Strumpshaw Fens.

6.3.2 Annual CH_4 emissions

Annual terrestrial CH_4 fluxes were reconstructed using regression analysis to infill as CH_4 emission was not measured continuously throughout the 16 month sampling period. As for annual CO_2 fluxes, spatial variation in plant community was incorporated into the model as to improve model performance (Kettunen et al., 2000, Laine et al., 2007b, Laine et al., 2009), resulting in mixed-effects models being used due to the lack of sufficient data arising from issues with ebullition (section 5.3) to parameterise individual collar models.

6.3.2.1 Reconstructed fen CH_4 emissions

Correlation coefficients for independent variables and CH_4 are shown in Table 31 in section 4.3.6. Dependent and independent variables transformations are shown in Table 49. The best CH_4 infill model found did not have site as a fixed effect but included collar

as a random effect (Table 50). The model had standardised peat temperature squared (ZPT2; Figure 80A), standardised barometric pressure (ZBaro; Figure 80B), ZBaro squared (ZBaro2) and standardised wind speed (ZWS) as independent variables. The standardised within group residuals were normally distributed (Figure 81B) and there were no substantial deviations from homogeneity seen in the data (Figure 81A).

Table 49 Independent variable shortlist post analysis for collinearity and their transformations.

Independent variable	Transformation
Peat temperature (PT)	$(PT+0.01)^2$
Water level (WL)	$(WL+0.01)^2$
VGA	$VGA^{0.33}$
Barometric pressure (Baro)	$(Baro+0.01)^2$
Wind speed	$WS^{0.6}$
Relative humidity	$RH^{0.6}$
CH_4 flux (dependent variable)	$Log(logCH_4+1)$

Annual CH_4 emission estimates were reconstructed for each collar using the mixed-effect model in Table 51. The average annual fluxes varied between collars (Table 52; Figure 82), with a greater range in reconstructed fluxes at Sutton (13 to 27 g CH_4 m^{-2} yr^{-1}) than at Strumpshaw fen (8.7 to 22 g CH_4 m^{-2} yr^{-1}). Sutton had a higher average annual flux (average of all collars; 18 ± 2.6 g CH_4 m^{-2} yr^{-1}) than Strumpshaw (15 ± 1.7 g CH_4 m^{-2} yr^{-1}). Collar 2 at Sutton fen had the highest reconstructed hourly flux (44 mg CH_4 m^{-2} h^{-1}), coinciding with the greatest reconstructed annual flux (27 g CH_4 m^{-2} yr^{-1}). Collar 5 and 6 at Strumpshaw fen were the collars with the second highest reconstructed hourly fluxes (both 24 mg CH_4 m^{-2} h^{-1}).

Table 50 Model selection and comparison using ΔAICc, AICc, -loglik and AICcweight for log(logCH4) (response variable). Predictor variables include standardised peat temperature (ZPT), standardised peat temperature squared (ZPT2), standardised barometric pressure (ZBaro), standardised barometric pressure squared (ZBaro2), standardised water level (ZWL), standardised water level squared (ZWL2), standardised vascular green area square-root transformed (ZVGA33) and standardised wind speed (ZWS). Collar was included as a random effect (1|c).

Model	-loglik	- loglik df	AICc	ΔAICc	AICcweight
ZPT2 + ZBaro + ZBaro2 + ZWS + (1|c)	62.83	7	141.05	0	0.61
ZPT2 + ZBaro + ZBaro2 + (1|c)	65.55	6	144.12	3.07	0.13
ZPT2 + ZBaro + ZBaro2 + ZVGA33 + (1|c)	65.47	7	146.31	5.26	0.04
ZPT2 + ZBaro + ZBaro2 + ZWL + (1|c)	65.49	7	146.35	5.30	0.04
ZPT2 + ZBaro + ZBaro2 + ZWL2 + (1|c)	65.52	7	146.41	5.36	0.04
ZPT + ZPT2 + ZBaro + ZBaro2 + (1|c)	65.55	7	146.48	5.43	0.04
ZPT2 + ZBaro + ZBaro2 + ZWL + ZWL2 + (1|c)	64.61	8	147.02	5.97	0.03
ZPT + ZPT2 + ZBaro + ZBaro2 + ZWL + (1|c)	65.48	8	148.77	7.71	0.01
ZPT + ZPT2 + ZBaro + ZBaro2 + ZWL2 + (1|c)	65.51	8	148.83	7.78	0.01
ZPT + ZPT2 + ZBaro + ZBaro2 + ZWL + ZWL2 + (1|c)	64.45	9	149.36	8.31	0.01
ZPT + ZPT2 + ZBaro + ZBaro2 + ZWL + ZWL2 + ZVGA33 + (1|c)	64.60	9	149.48	8.43	0

Table 51 Summary statistics for the model created using ME GLM, where log(logCH4) is the response variable; ZPT2 (standardised peat temperature squared), ZBaro (Standardised barometric pressure), ZBaro2 (ZBaro squared) and ZWS (standardised wind speed$^{0.6}$) are the independent variable (no site fixed effect) and the model has the same slope for both sites but with random variation (intercept) between collars.

Equation:	$\log(logCH4) = a \cdot b \cdot ZPT2 + c \cdot ZBaro + d \cdot ZBaro2 + e \cdot ZWS + (1\|collar)$			
		-loglik $_7$ = 62.83		
Random effects:				
Formula: = 1|collar	Intercept	Residual		
Std. Dev.	0.2078	0.4825		
Sutton	Intercept		Strumpshaw	Intercept
1	-0.36		1	-0.73
2	-0.10		2	-0.37
3	-0.41		3	-0.45
4	-0.51		4	-0.34
5	-0.38		5	-0.19
6	-0.49		6	-0.33
	Value	Std. error	DF	t-test
(Intercept)	-0.39	0.33	74	-1.2
ZPT2	0.80	0.20	74	4.0
ZBaro	2.1	1.1	74	1.9
ZBaro2	-1.9	0.94	74	-2.0
ZWS	-0.62	0.304	74	-2.0

To evaluate the models predicted versus observed CH_4 fluxes were plotted (Figure 83) and analysed for a linear pattern. A clear linear pattern is observed, with each collar slope plotted for Sutton (Figure 83A) and Strumpshaw fen (Figure 83B). Furthermore, model sensitivity analysis was performed on the reconstructed annual flux by varying environmental variables by ± 10 %. A high sensitivity (≥ 10 % or ≤ -10% response) was observed for barometric pressure (Figure 84), but not for peat temperature and wind speed (< 10 % and > -10 %).

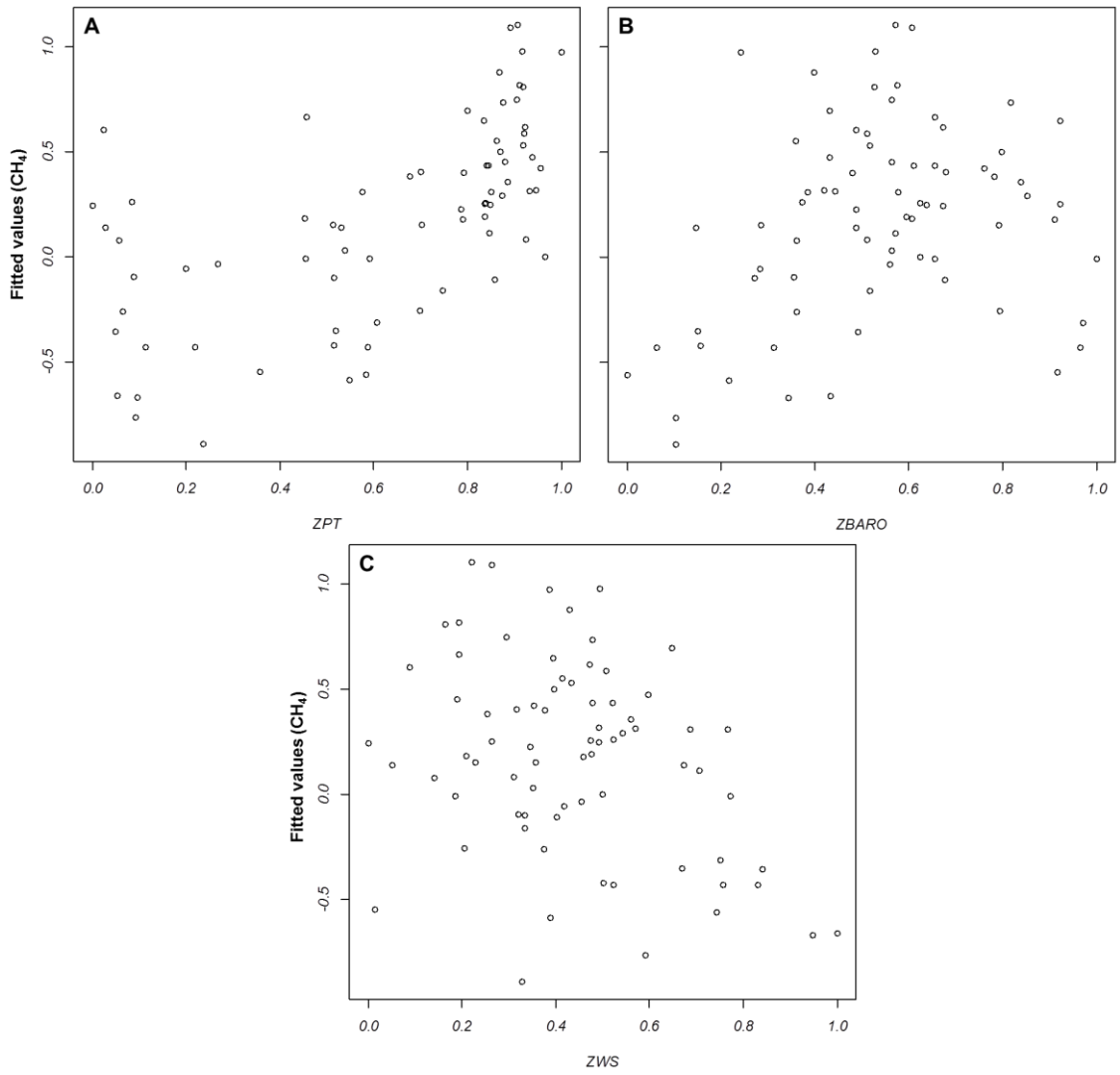


Figure 80 Scatter plot of fitted CH_4 values and (A) ZPT, (B) ZBaro and ZWS (C).

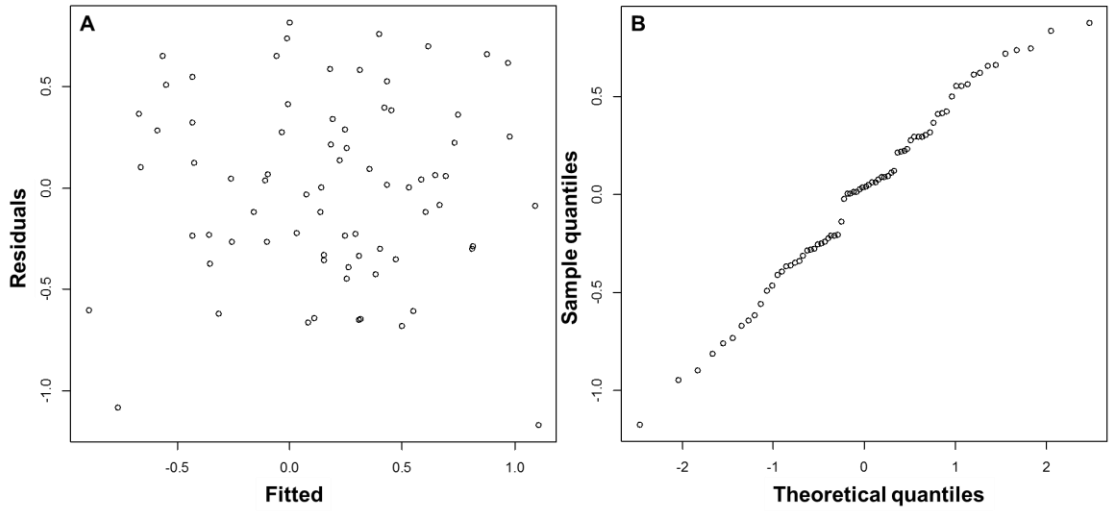


Figure 81 Validation plot (A) of residuals vs. fitted values (log(logCH_4)) to test the assumptions of homogeneity and Q-Q plot (B) of residuals from the optimal model to test the assumption of normality.

Table 52 Reconstructed methane flux statistics for each collar form 1st September 2012 to 31st August 2013.

Site	Collar	Annual flux (g CH_4 m^{-2} yr^{-1})	Hourly CH_4 fluxes (mg CH_4 m^{-2} h^{-1})			
			Mean	Standard error	Minimum	Maximum
Sutton	1	17	1.9	0.02	0.06	18
	2	27	3.1	0.03	0.08	44
	3	15	1.7	0.01	0.06	16
	4	13	1.5	0.01	0.05	12
	5	25	2.9	0.03	0.08	21
	6	13	1.5	0.01	0.05	12
Strumpshaw	1	8.7	1.0	0.01	0.04	7.8
	2	16	1.8	0.02	0.05	21
	3	13	1.5	0.01	0.05	16
	4	16	1.9	0.02	0.05	23
	5	22	2.5	0.03	0.06	24
	6	17	1.9	0.02	0.05	24

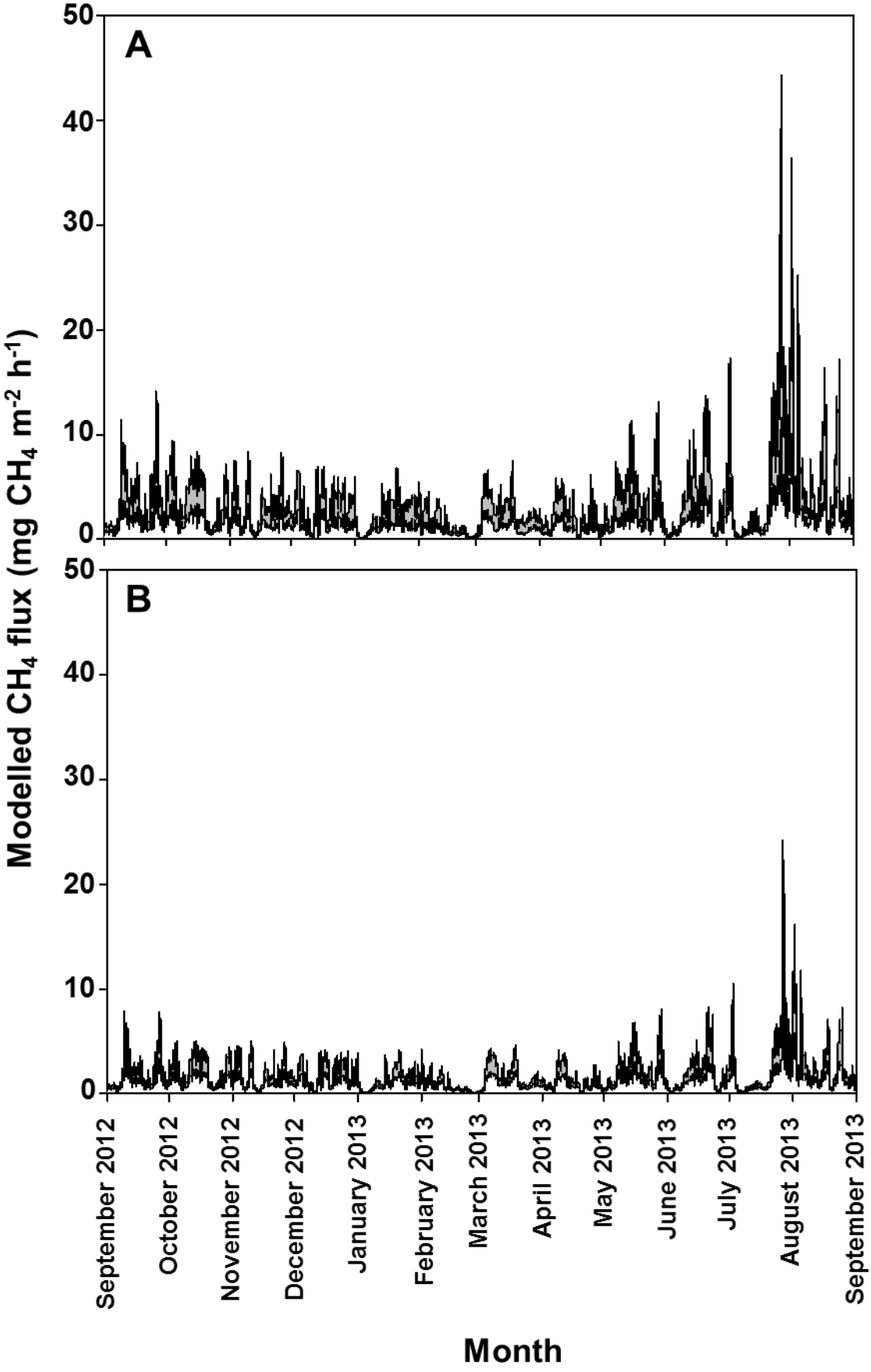


Figure 82 Reconstructed CH_4 emissions for all collars (minima and maxima shown) for Sutton (A) and Strumpshaw Fen (B).

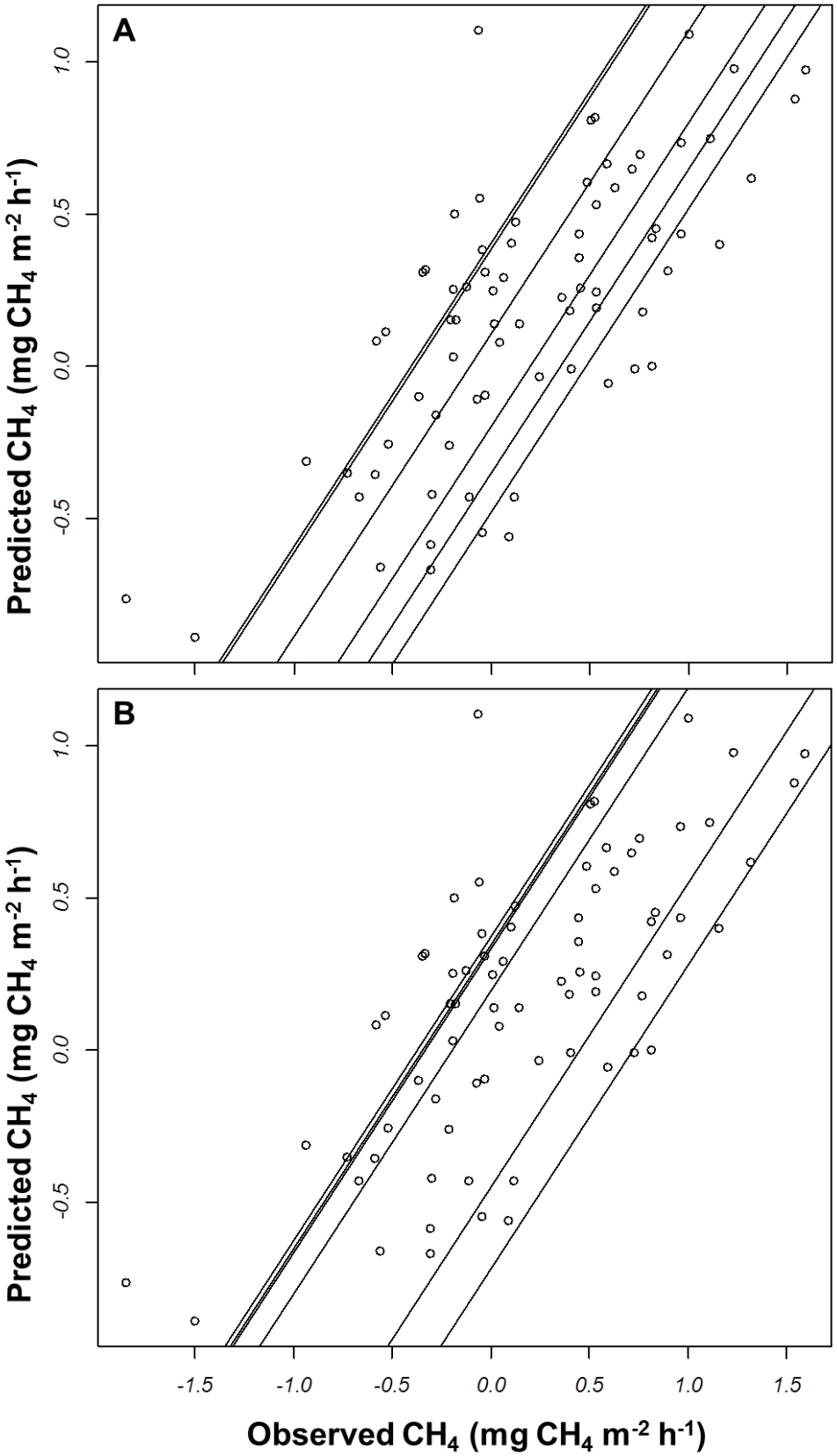


Figure 83 Plot of observed versus predicted CH_4 hourly flux for Sutton (A) and Strumpshaw (B). The 1:1 line is shown with the corresponding intercept for each collar.

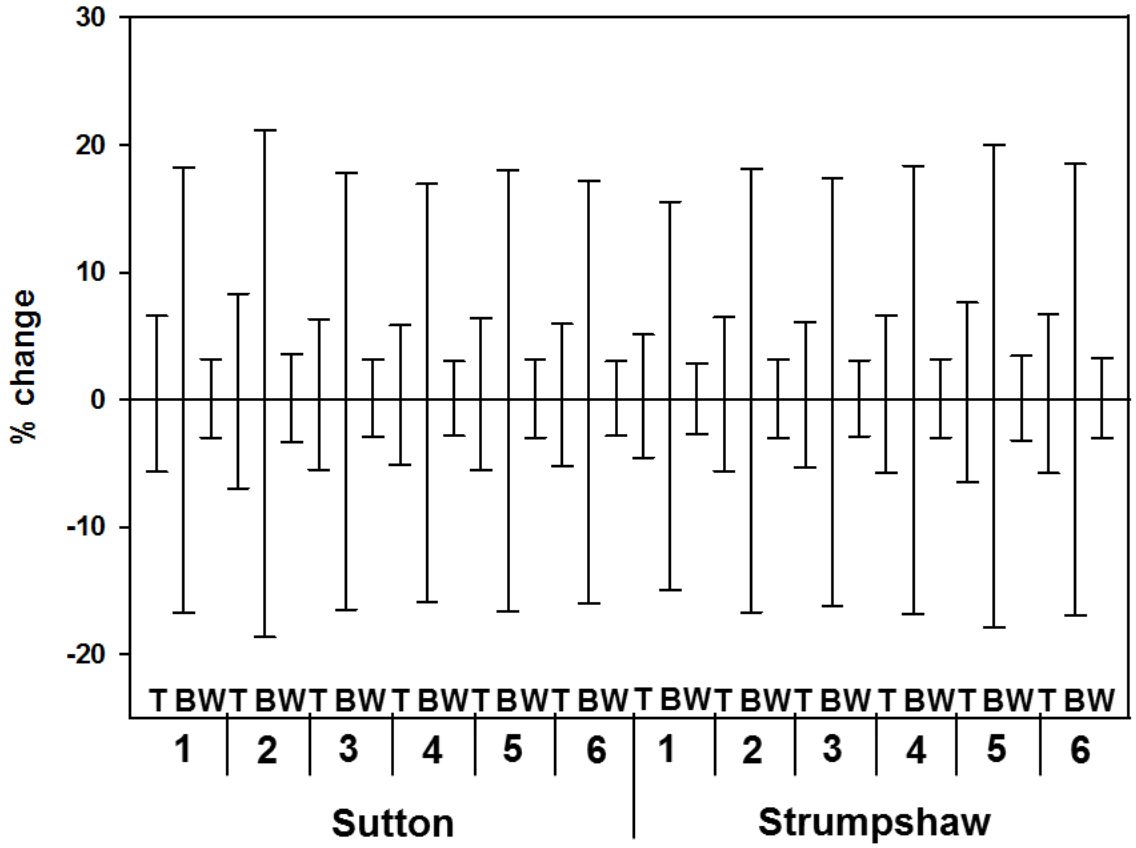


Figure 84 Sensitivity analyses of model parameters peat temperature (T; ˚C), barometric pressure (B; kPa) and wind speed (W; m s^{-1}) in relation to annual CH_4 flux (g CH_4 m^{-2} yr^{-1}) for each collar at Sutton and Strumpshaw Fens. Each parameter was varied by ± 10 %.

6.3.2.2 Reconstructed ditch CH_4 emissions

To ascertain the importance of ditches as sources within floodplain fens due to the greater observed fluxes in section 4.3 (generally by an order of magnitude), annual CH_4 was reconstructed, despite the low number of replicate measurements. It is acknowledged that due to the low number of replicates, any reconstructed ditch fluxes will be uncertain; however, it gave a rough estimate of the range in annual fluxes between sites. Results will not be included in a total site flux, only for comparison between site and the relative importance of aquatic (ditch) and terrestrial (fen) CH_4 emission (section 6.5). The same steps were taken as in section 6.2.1 for ditch CH_4 infill modelling: the dependent variable was normalised and correlated with independent variables (Table 53) and a shortlist of independent variables are shown in Table 54, along with their transformations.

Table 53 Spearman's rank correlation for ditch CH_4 flux and selected independent variables (air temperature (AT; ºC), peat temperature (PT; ºC), barometric pressure (Baro; kPa), relative humidity (RH; %), wind speed (WS; m s^{-1}) and photosynthetically active radiation (PAR; µmol m^{-2} s^{-1})). * and ** indicate the correlation is significant at the 0.05 and < 0.001 level.

	CH_4	PT	AT	Baro	RH	WS	PAR
CH_4							
PT	0.42*						
AT	0.42*	0.88**					
Baro	0.11	0.18	0.27				
RH	0.1	-0.12	-0.33*	-0.23			
WS	0.21	0.15	0.23	-0.03	-0.13		
PAR	0.18	0.4*	0.53**	0.49**	-0.5**	0.34**	

Table 54 Independent variable shortlist post analysis for collinearity and their transformations.

Independent variable	Transformation
Peat temperature (PT)	PT^2
PAR	$PAR^{0.4}$
Barometric pressure (Baro)	$Baro^2$
Wind speed	$WS^{0.6}$
Relative humidity	RH
CH_4 flux (dependent variable)	$LogCH_4$

The best model (Table 55) was selected using delta AICc. The best model found did not have site as a fixed effect but included site as a random effect (Table 56). The model had standardised peat temperature squared (ZPT2; Figure 85A), standardised barometric pressure (ZBaro; Figure 85B) and ZBaro squared (ZBaro2) as independent variables. The standardised within group residuals were normally distributed (Figure 86B) and there were no substantial deviations from homogeneity seen in the data (Figure 86A).

Table 55 Model selection and comparison using ΔAICc, AICc, -loglik and AICcweight for logCH4 (response variable). Predictor variables include standardised peat temperature (ZPT), standardised peat temperature squared (ZPT2), standardised barometric pressure (ZBaro), standardised barometric pressure squared (ZBaro2), standardised PAR transformed (ZPAR2), standardised wind speed (ZWS) and standardised wind speed squared (ZWS2). Site was included as a random effect (1|Site).

Model	- loglik	- loglik df	AICc	ΔAICc	AICcweight
ZPT2 + ZBARO + ZBARO2 + (1|Site)	83.10	6	180.24	0	0.19
ZPT2 + ZBARO + ZBARO2 + ZWS + ZWS2 + ZPAR2 + (1|Site)	79.26	9	181.25	1.01	0.12
ZPT2 + ZPAR2 + (1|Site)	85.19	5	181.81	1.56	0.09
ZPT2 + ZBARO2 + (1|Site)	85.32	5	182.07	1.83	0.08
ZPT + ZPT2 + (1|Site)	85.39	5	182.21	1.97	0.07
ZPT2 + ZWS + ZWS2 + (1|Site)	84.13	6	182.30	2.06	0.07
ZPT2 + ZWS2 + (1|Site)	85.59	5	182.60	2.36	0.06
ZPT2 + ZBARO + ZBARO2 + ZWS2 + (1|Site)	82.97	7	182.74	2.50	0.06
ZPT + ZPT2 + ZBARO + ZBARO2 + (1|Site)	83.05	7	182.91	2.66	0.05
ZPT2 + ZBARO + ZBARO2 + ZWS + (1|Site)	83.07	6	182.93	2.69	0.05
ZPT + ZPT2 + ZPAR2 + (1|Site)	84.90	8	183.85	3.60	0.03
ZPT + ZPT2 + ZWS + ZWS2 + (1|Site)	83.65	6	184.10	3.86	0.03
ZPT + ZPT2 + ZBARO2 + (1|Site)	85.15	8	184.34	4.10	0.03
ZPT2 + ZBARO + ZBARO2 + ZWS + ZWS2 + (1|Site)	82.36	6	184.42	4.18	0.02
ZPT + ZPT2 + ZWS2 + (1|Site)	85.36	8	184.77	4.53	0.01
ZPT + ZPT2 + ZBARO + ZBARO2 + ZWS2 + (1|Site)	82.96	8	185.62	5.38	0.01
ZPT + ZPT2 + ZBARO + ZBARO2 + ZWS + (1|Site)	82.34	9	187.42	7.18	0.01

Table 56 Summary statistics for the model created using ME GLM, where log(logCH4) is the response variable; ZPT2 (standardised peat temperature squared), ZBaro (Standardised barometric pressure) and ZBaro2 (ZBaro squared) are the independent variable and the model has the same slope for both sites but with random variation (intercept) between sites.

Equation: $logCH4 = a \cdot ZPT2 + b \cdot ZBaro + c \cdot ZBaro2 + (1\|Site)$				
		-loglik = 83.10		
Random effects:				
Formula: = 1|Site	Intercept	Residual		
Std. Dev.	0.2078	0.4825		
Site	Intercept			
Sutton	2.874023			
Strumpshaw	0.127527			
	Value	Std. error	DF	t-test
(Intercept)	1.5008	1.3537	48	1.109
ZPT2	3.9286	0.5958	48	6.594
ZBaro	-6.6107	3.0621	48	-2.159
ZBaro2	5.8545	2.5592	48	2.288

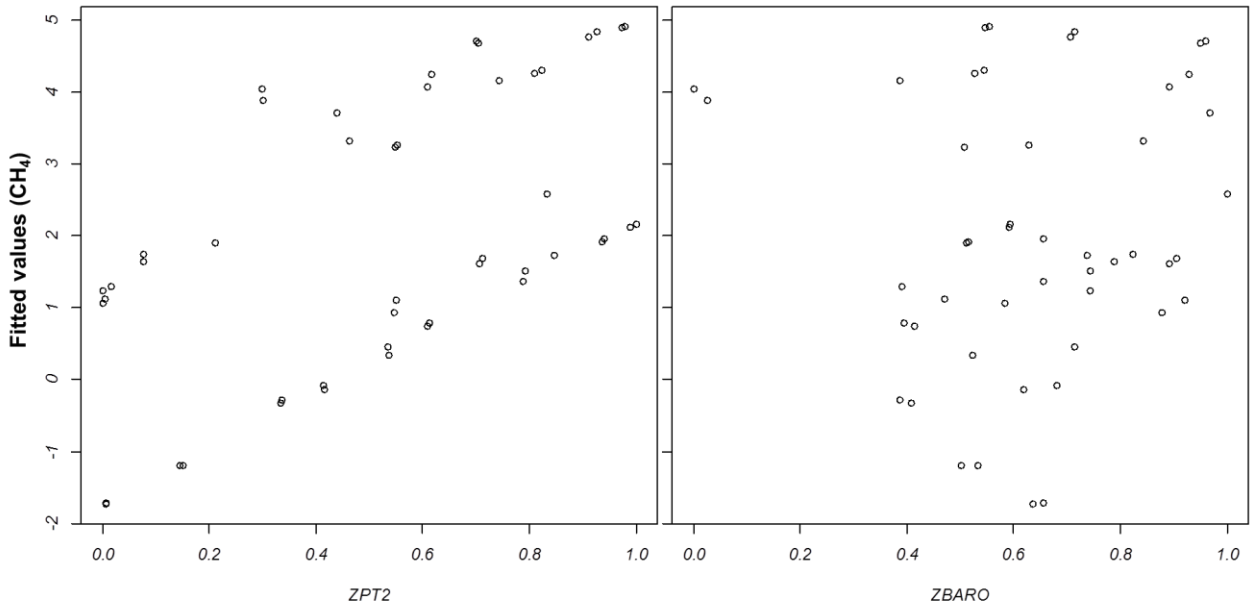


Figure 85 Scatter plot of fitted CH_4 values and (A) ZPT and (B) ZBaro.

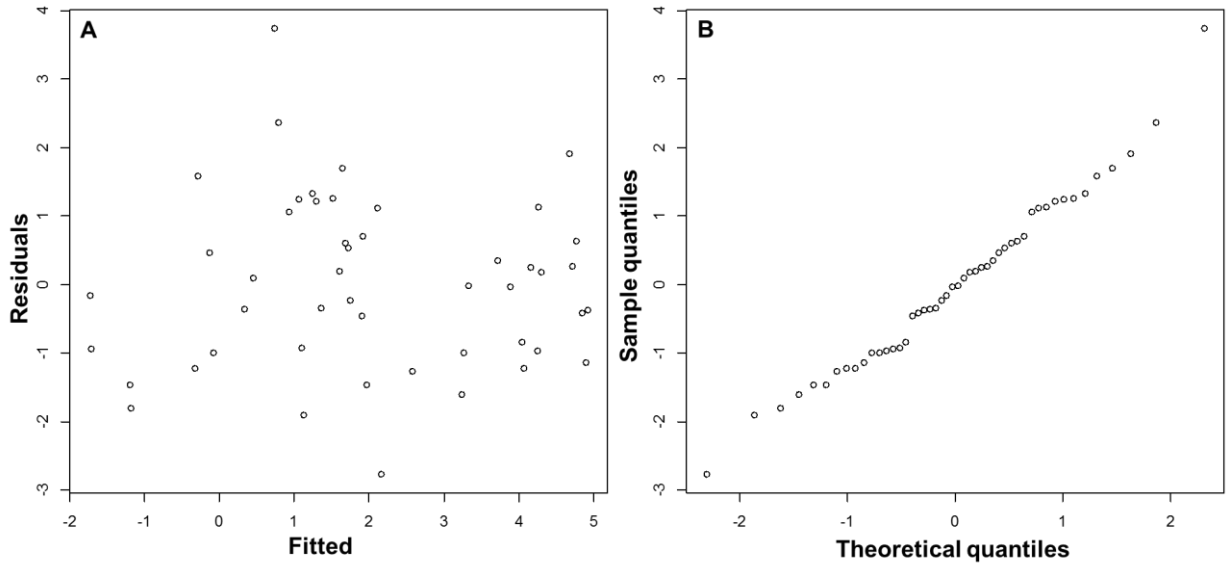


Figure 86 Validation plot (A) of residuals vs. fitted values ($logCH_4$) to test the assumptions of homogeneity and Q-Q plot (B) of residuals from the optimal model to test the assumption of normality.

Annual ditch CH_4 flux (Figure 87) estimates were reconstructed for each collar using the mixed-effect model in Table 56. The average annual ditch fluxes varied between ditches (Table 57), with a greater range in reconstructed fluxes at Sutton (6671 to 26835 g CH_4 m^{-2} yr^{-1}) than at Strumpshaw fen (138 to 147 g CH_4 m^{-2} yr^{-1}). Sutton had a significantly higher average annual flux (Table 44; average of both ditches: 16753 ± 10082 g CH_4 m^{-2} yr^{-1}) than Strumpshaw (143 ± 4.7 g CH_4 m^{-2} yr^{-1}).

Table 57 Reconstructed ditch methane flux statistics for each collar form 1st September 2012 to 31st August 2013. Fluxes were significantly greater at Sutton Fen than Strumpshaw Fen (t_2 = 80.495, p < 0.001).

Site	Collar	Annual flux (g CH_4 m^{-2} yr^{-1})	Hourly CH_4 fluxes (mg CH_4 m^{-2} h^{-1})			
			Mean	Standard error	Minimum	Maximum
Sutton	1	26835	3064	274	3.0	680965
	2	6671	762	45	2.9	87294
Strumpshaw	1	147	17	1.5	0.01	3461
	2	138	16	1.4	0.01	3244

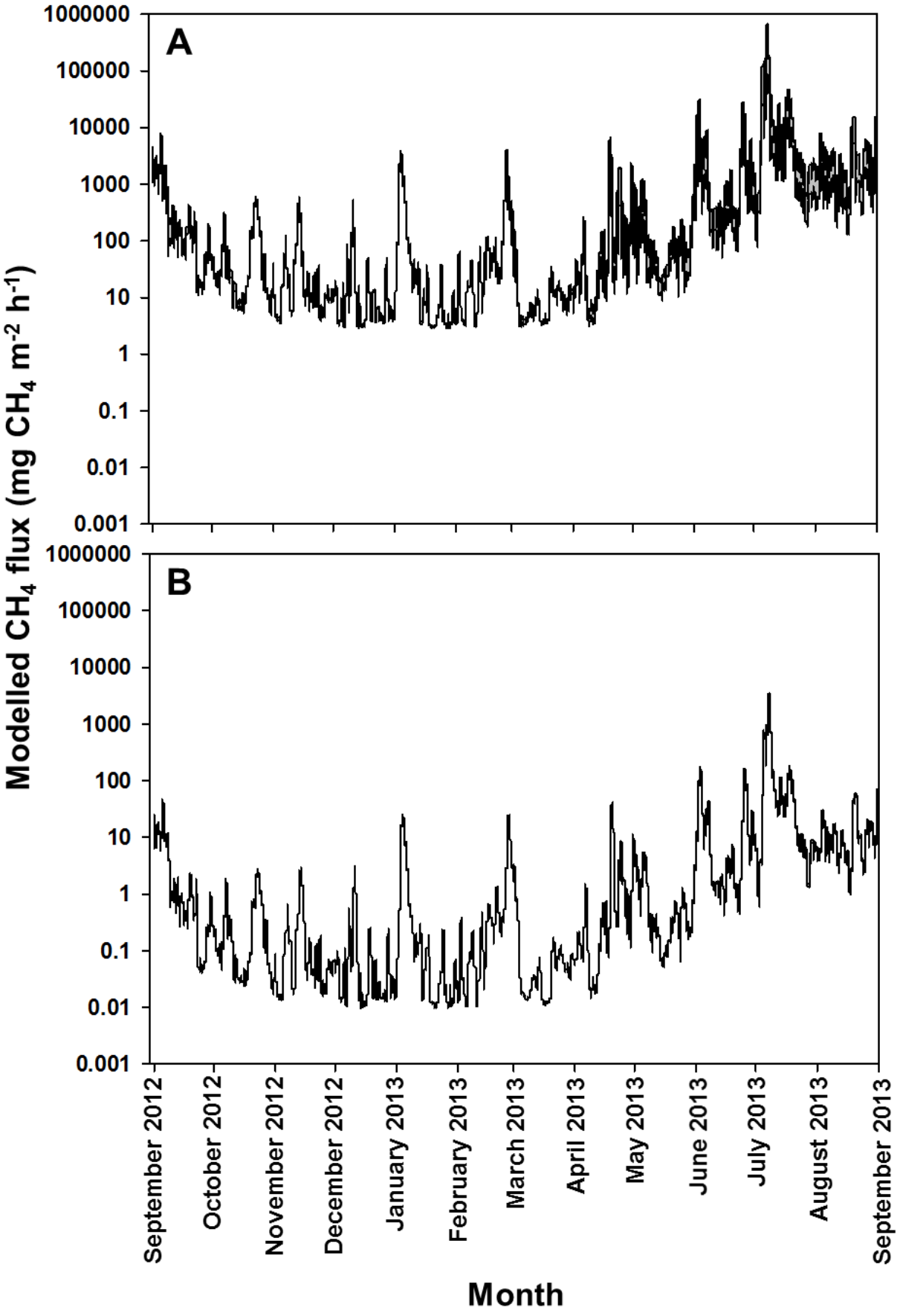


Figure 87 Reconstructed fluxes for all ditches (minima and maxima shown) for Sutton (A) and Strumpshaw Fen (B). Note logarithmic scale.

To evaluate the models predicted versus observed CH_4 fluxes were plotted (Figure 88) and analysed for a linear pattern. A clear linear pattern is observed, with each site slope plotted. Some of the larger ditch fluxes may be underestimated (Figure 88). Furthermore, model sensitivity analysis was performed on the reconstructed annual flux by varying environmental variables by ± 10 %. A high sensitivity (≥ 10 % or ≤ -10% response) was observed for all parameters (Figure 89).

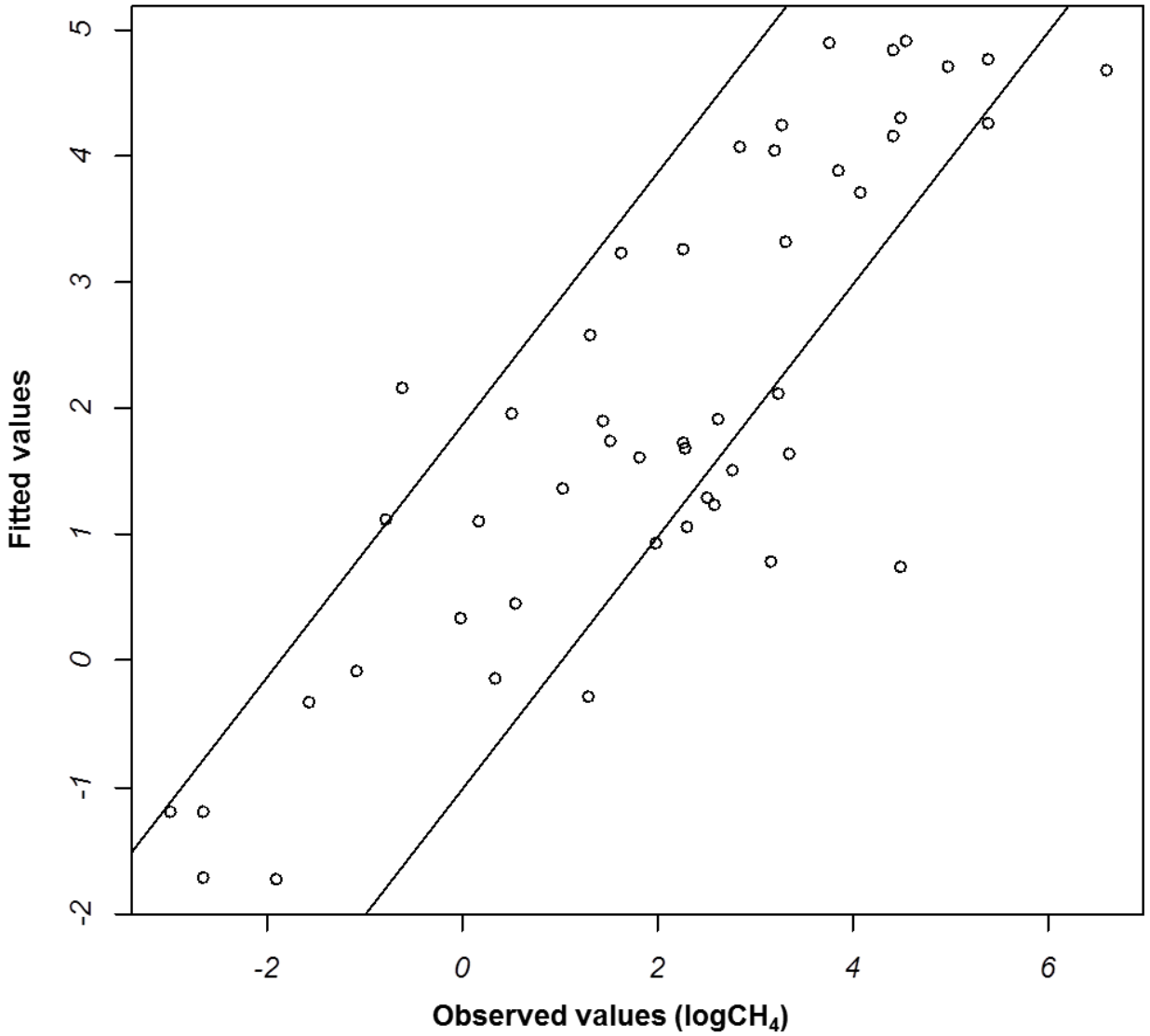


Figure 88 Plot of observed versus predicted CH_4 hourly flux for Sutton (A) and Strumpshaw (B). The 1:1 line is shown with the corresponding intercept for each collar.

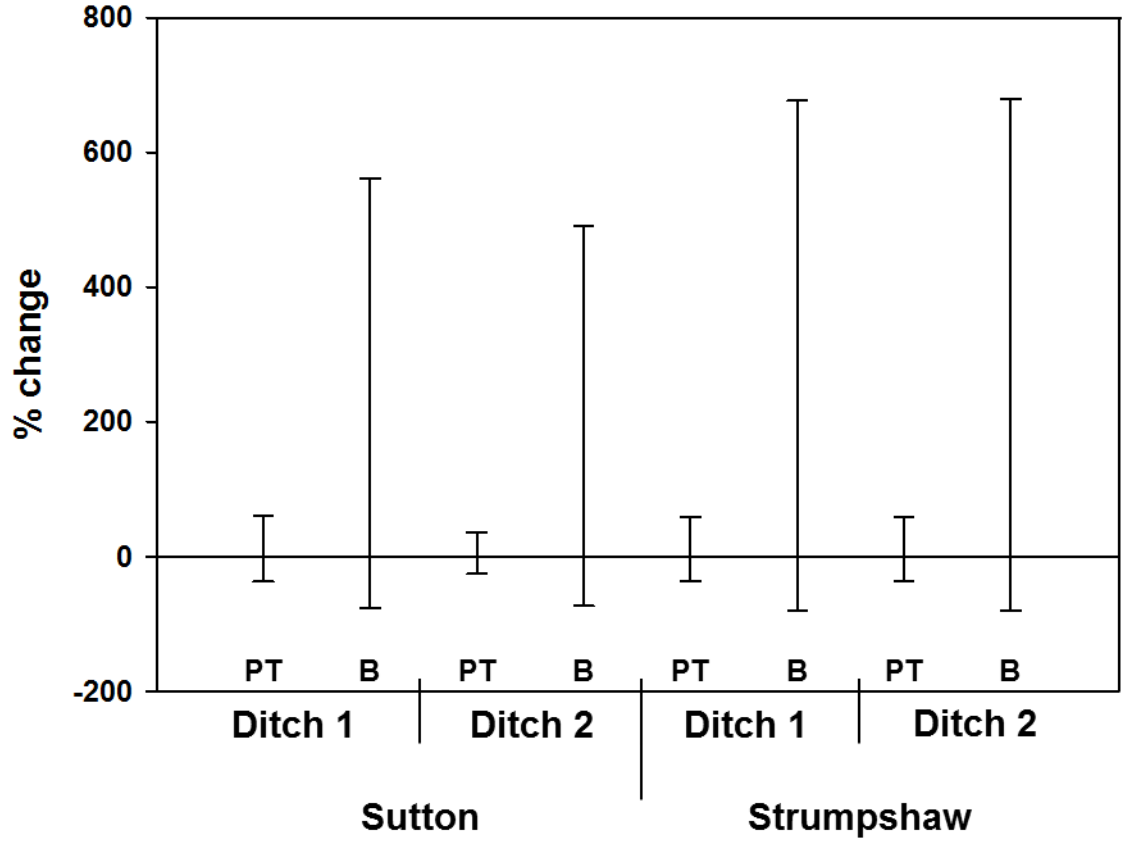


Figure 89 Sensitivity analyses of model parameters peat temperature (PT; ˚C) and barometric pressure (B; kPa) in relation to annual ditch CH_4 flux (g CH_4 m^{-2} yr^{-1}) for each collar at Sutton and Strumpshaw Fens. Each parameter was varied by ± 10 %.

6.4 CO_2-equivalent fluxes for Sutton and Strumpshaw Fen

GWPs were used to calculate a C flux for both gaseous CO_2 and CH_4 fluxes. The total C flux was calculated using the conversion factors in Ramaswamy et al. (2001) to convert annual reconstructed CH_4 fluxes to CO_2-equivalents over a 20, 100 and 500 year period (Table 58). Strumpshaw Fen was a significantly greater C sink than Sutton Fen between 1st September 2012 and 31st August 2013 over a 20-, 100- and 500-year period ($t_{6.221}$ = 3.1546, p = 0.019; $t_{5.709}$ = 3.2546, p = 0.019; and $t_{5.716}$ = 3.2961, p = 0.018, respectively). Annual CH_4 emissions were significantly higher than CO_2 exchange ($t_{13.131}$= -5.8537, p < 0.001; $t_{11.365}$= -4.2005, p < 0.001; $t_{11.029}$= -3.216, p = 0.008; over 20-, 100- and 500-year period, respectively).

Table 58 Summary of annual terrestrial C exchange (CO_2 and CH_4) expressed as CO_2-equivalents ± 1 S.E. Annual CH_4 fluxes were multiplied by 62, 25 and 7 to convert into CO_2-equivalent fluxes over a 20-, 100- and 500-year period (Drewer et al., 2010).

Site	Gas	Annual reconstructed flux (g CO_2/CH_4 m^{-2} yr^{-1})	CO_2-equivalent flux (g CO_2-equivalent m^{-2} yr^{-1})		
			20-year period	100-year period	500-year period
Sutton	CO_2	-90 ± 139	-90 ± 139	-90 ± 139	-90 ± 139
	CH_4	18 ± 2.6	1138 ± 159	459 ± 64	128 ± 18
	Total		1048 ± 174	331 ± 119	1 ± 114
Strumpshaw	CO_2	-1560 ± 418	-1560 ± 418	-1560 ± 418	-1560 ± 418
	CH_4	15 ± 1.7	957 ± 108	386 ± 44	108 ± 12
	Total		-603 ± 494	-1174 ± 447	-1452 ± 426

6.5 Relative importance of aquatic and terrestrial CH_4 emissions

Observed CH_4 emissions reported in section 4.3 showed ditch fluxes to be significantly greater than fen fluxes and therefore scaled CH_4 per surface area were investigated. Scaled CH_4 emissions according to the fen and ditch surface area are shown in Table 45. Scaled CH_4 fluxes were significantly greater in ditches than in the fen for both Sutton (t_1 = -21.622, p = 0.035) and Strumpshaw Fen (t_1 = -26.142, p = 0.024).

Table 59 Ditch and fen area (km^2) and scaled up annual fluxes for ditch and fen (Mg CH_4 yr^{-1}).

Site	Total site area (km^2)	Ditch area		Fen area		Scaled fluxes		Total annual flux
		km^2	%	km^2	%	Ditch	Fen	
Sutton	0.782	0.031	4	0.752	96	519 ± 313	14 ± 1.9	533 ± 315
Strumpshaw	0.775	0.165	21	0.372	48 [a]	24 ± 0.77	5.7 ± 0.65	29 ± 1.4

[a] 31 % of Strumpshaw Fen (0.24 km^2) is covered in fen carr and fen fluxes are not representative for this ecosystem type.

6.6 Discussion

This chapter investigated annual C exchange from two lowland floodplain fens using the following research questions and hypotheses:

R.Q.5. Over a one year period, what are the integrated annual fluxes for CO_2 and CH_4 from the two floodplain fens?

H_8: Strumpshaw Fen will have greater annual fluxes for GPP, R_{eco} and CH_4.

R.Q.6. What are the CO_2 equivalent GHG fluxes for each GHG for Sutton and Strumpshaw fens?

H_9: CH_4 will have a greater CO_2-equivalent flux than CO_2 at both sites.

H_{10}: Strumpshaw Fen will be a greater sink of C than Sutton Fen.

6.6.1 Reconstructed annual C exchange in sites of differing nutrient status

Reconstructed annual fen R_{eco}, GPP and CH_4 fluxes varied temporally and spatially at Sutton and Strumpshaw Fen. Annual R_{eco} and GPP fluxes were significantly greater at Strumpshaw Fen between 1st September 2012 and 31st August 2013. No significant difference in CH_4 fluxes were observed between sites, resulting in H_8 being partially accepted.

The significantly greater CO_2 fluxes at Strumpshaw Fen were anticipated due to the significantly greater aboveground green biomass and porewater nutrient concentrations than at Sutton Fen. The VGA was shown to be an important controlling factor on GPP and R_{eco} in section 4.3.6 (Table 33). A greater green photosynthesising area allows for greater CO_2 assimilation (Laine et al., 2007a, Riutta et al., 2007a). Differences in pmax (variation between collars; Table 45) in the GPP model account for differences in plant species composition within each collar and their efficiency at sequestering CO_2. GPP varied temporally with the greatest uptake of CO_2 during the summer months, especially at Strumpshaw Fen. A small amount of GPP occurred at Sutton Fen during the winter due to the evergreen properties of *C. mariscus* and *J. subnodulosus*. Greater CO_2 assimilation rates and aboveground biomass have the potential to increase root exudate release and provide greater quantities of labile C for R_{eco} (Badri and Vivanco, 2009). No *in situ* study has quantified CO_2 emissions derived from root exudate release; however,

a couple of *ex situ* mesocosm studies have shown that root exudate mineralisation can significantly contribute to R_{eco} (Silvola et al., 1996, Crow and Wieder, 2005, Basiliko et al., 2012). In addition, greater aboveground biomass has been shown to increase rhizosphere oxidation and subsequently, greater R_{eco} (Armstrong et al., 1992, Brix et al., 1996, Chanton, 2005, Ström et al., 2005).

The significantly greater porewater NO_3^- and SRP concentrations at Strumpshaw Fen than at Sutton Fen (Table 16, section 3.3.6) caused greater R_{eco} as the two macronutrients were found to be important controlling factors (Table 33, section 4.3.6). Previous *in situ* studies within mineral soils and *ex situ* studies within peat have shown both NO_3^- and SRP to increase mineralisation due to the greater reactants for microbes (Aerts and Toet, 1997, Amador and Jones, 1997, Min et al., 2011), corroborating with this study. Significantly greater porewater concentrations at Strumpshaw Fen than at Sutton Fen (Table 16) also caused greater GPP at Strumpshaw Fen than at Sutton Fen. SRP is often a growth limiting macronutrient in floodplain fens and SRP inputs will help to increase aboveground green biomass, in turn increasing CO_2 sequestration rates (Wassen and Olde Venterink, 2006, Koelbener et al., 2010). Greater foliar N contents have also been shown to increase photosynthetic uptake of CO_2 (Liu and Greaver, 2009). Foliar nutrient contents were not included in controlling factors analysis in chapter 4 as foliar nutrient contents were only established in September 2012 and not for every site visit. However, foliar N contents in 2012 were significantly greater at Strumpshaw Fen than at Sutton Fen and may have augmented GPP at the former site.

Differences in water level due to differences in site management may have also had an impact on CO_2 exchange between Sutton and Strumpshaw Fen, as water level was found to be a controlling factor on both R_{eco} and GPP (Table 33). A linear mixed-effects model (independent variable: Site, covariate: Month, random effect: collar) showed a significant difference in water level between sites ($F_{1,136} = 6.488$, $p = 0.012$) and month ($F_{13,136} = 86.928$, $p < 0.001$). No significant interaction terms between site and depth were observed. Variation between sites and collars were encapsulated within the R_{eco} model, with collar being a random effect on the scaling parameter for water level (b3; Table 44). No variation between collar or site water level was described in the annual GPP model (Table 45). The inclusion of spatial variability in water level for R_{eco} may be due to the greater importance of water level on R_{eco} than GPP (Table 33), as water level directly alters the portion of the peat profile where aerobic respiration can occur. GPP is not as

directly controlled by water level as species found within Sutton and Strumpshaw Fen are adapted to cope with waterlogged conditions. Little effect of the January and March 2013 flood events was observed in modelled CO_2 exchange at the time of the flood events (Figure 77).

Some error in the CO_2 exchange reconstruction models may be explained by measurements during the winter only being made at Sutton Fen in January. However, the inclusion of all data within the mixed-effects models used for both R_{eco} and GPP reconstruction allows the relationships between all variables and CO_2 fluxes to be established, even during the winter time. The winter month included in the analysis, January 2013, was colder than December 2012 and February 2013 and should therefore resolve any temperature variability for the two missing months within the reconstruction models. Therefore, the lack of winter time observed values does not merit the exclusion of any winter time reconstructed fluxes from the data set, especially when the reconstruction models had reasonable MEF values.

The GPP infill model was most sensitive to VGA; however, alterations by ± 10 % to the environmental variables did not alter fluxes more than 5 % of the original flux. This was not observed in the R_{eco} model, which was sensitive to alterations in peat temperature (> 10 % from the original R_{eco} annual estimate). This high sensitivity of the R_{eco} model to peat temperature are reflected in the significant correlation in Table 29. Peat temperature was shown to be a significant controlling factor on R_{eco} in section 4.3.6 as it regulates microbial activity (Huth et al., 2012, Kandel et al., 2013a, Kandel et al., 2013b). Changes from the original annual estimate were < 1.5 % for VGA and water level within the R_{eco} model. The GPP model was not as sensitive to alterations in PAR, air temperature and water level. The majority of VGA responses in GPP models within the literature do not include any other parameter as contributing to the VGA portion of the model, apart from a vegetation extinction coefficient (Kiene and Hines, 1995). Normally linear or exponential responses are used for VGA interactions on GPP (Laine et al., 2007a, Wilson et al., 2007a, Maanavilja et al., 2011); however, GPP modelling within this study showed how water level and air temperature modified the response of GPP to VGA in floodplain fen sites (Table 45). This corroborates with controlling factor analysis on GPP (section 4.3.6), with air temperature and water level being the two controlling factors that have the highest relative importance after VGA. Presently, no previous peatland study

has shown air temperature and water level to modify the response of GPP to VGA within a GPP model.

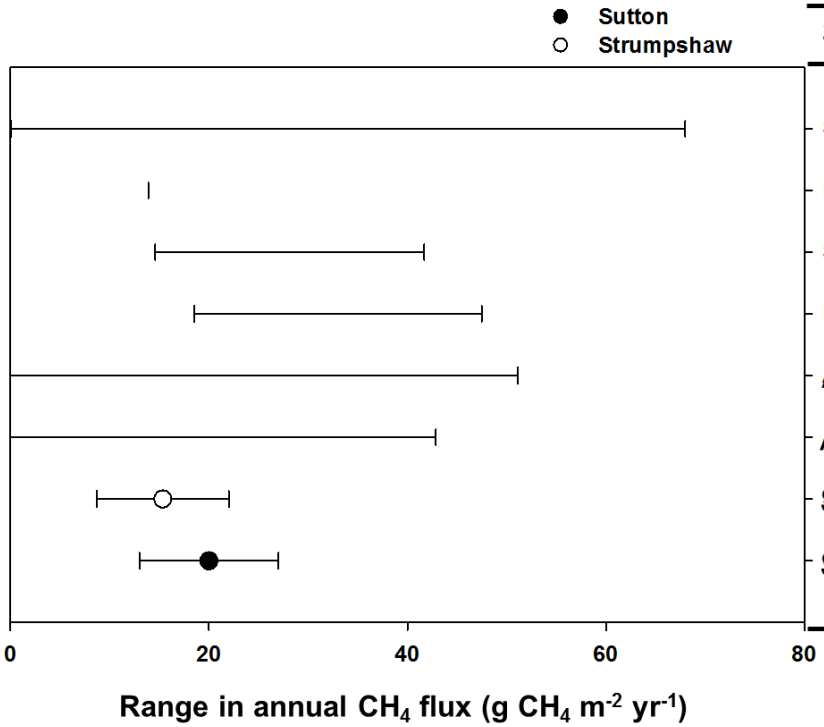
The lack of difference between sites in annual CH_4 flux was not anticipated (H_8) as it was thought that prior to the study a difference in nutrient status alters CH_4 emission. Controlling factor analysis (Table 33) showed both NO_3^- and SRP to have an impact on CH_4 emission. However, the low relative importance of the two macronutrients (10 and 3 % for NO_3^- and SRP, respectively) may translate into the lack of difference in annual CH_4 emission between Sutton and Strumpshaw Fen, with other environmental factors playing a larger role in CH_4 emission, such as peat temperature, water level, etc. (Table 33). Modelling for infilling revealed that collar has an effect on emission. This illustrates the heterogeneous nature of peatlands, as also observed in Hendriks et al. (2007), Schrier-Uijl et al. (2010b) and Koch et al. (2014). The infill method used in this study is not a universal method, with many previous studies using linear interpolation between site visits or in missing eddy covariance data to quantify an annual CH_4 flux (Rinne et al., 2007, Lohila et al., 2011). Infill modelling using regression analysis allows for the quantification of relationships between dependent and independent variables. These relationships can then be used to model data in between sampling dates and give more reliable estimates than purely linearly interpolating between two points (Alm et al., 2007).

Annual reconstructed terrestrial CH_4 fluxes were within the annual fluxes reported in the literature (Figure 90). A number of factors are attributed to the difference in reconstructed terrestrial fluxes between studies. Firstly, the exclusion of ebullitive and ditch fluxes from the annual CH_4 emissions from Sutton and Strumpshaw Fen result in lower fluxes than if these two transport pathways were included. The meteorological conditions over the year varied significantly. The winter months (December 2012 to February 2013) and March 2013 were exceptionally wet, with a number of heavy rainfall events exceeding 20 mm d^{-1} (Figure 23; Met Office (2013)). Additionally, summer 2013 months (June to September) were warmer than the 30 preceding year average. Billett et al. (2015) by contrast experienced the wettest summer in 30 years in 2011, resulting in cooler temperatures than the long-term records. These cooler conditions result in smaller fluxes as temperature is a controlling factor on methanogenesis (Le Mer and Roger, 2001, Lai, 2009). Additionally, in Hendriks et al. (2007) and Schrier-Uijl et al. (2010b) the vegetation was cut during the sampling period, which will alter root exudate release into the peat and reduce the labile C source for methanogenesis (Ryan, 1991, Badri and Vivanco,

2009). As vegetation is cut, dominance is placed on above-ground biomass production rather than below-ground biomass, reducing root exudate release (Ryan, 1991). At Sutton and Strumpshaw Fen, the vegetation was not cut during the sampling period, allowing for normal above- and below-ground biomass production for the different plant species observed at the two sites and root exudate release for r-strategist methanogens, microbes that proliferate on labile organic C (Ryan, 1991), to utilise. K-strategist microbes decompose more recalcitrant OM (Ryan, 1991). Root exudates were not measured in this study.

The difference in vegetation type may account for differences in reconstructed annual fluxes in Audet et al. (2013a) and Audet et al. (2013b). *A. stolinifera* does not grow as tall as *P.* australis, only to a maximum height of 1 m (Grime et al., 2007). The peat substrate within the Danish riparian sites was also different to Sutton and Strumpshaw Fen, with a mix between peat and sandy layers throughout the profile. These layers of mineral material alter the peat structure, potentially enabling greater passage of CH_4 gas bubble in the form of steady ebullition.

Annual fluxes for Sutton and Strumpshaw Fens showed a similar seasonal pattern to observed fluxes (Figure 51 and 82). The seasonal pattern is thought to be due to temperature, which has been shown in other studies (Hendriks et al., 2007, Schrier-Uijl et al., 2010b) and with controlling factor analysis in section 4.3.6, increasing microbial activity. Additionally, the greater amount of incoming solar radiation during the summer (Figure 48) may increase the amount of root exudate release from plants which could potentially be used by methanogens as a labile carbon source (Badri and Vivanco, 2009). Root exudate release was not measured in this study; however, relationships between PAR and root exudate release have been demonstrated in peatlands (Nykanen et al., 1995, Thomas et al., 1996, Koelbener et al., 2010, Koebsch et al., 2013b) and in other environments (Ryan, 1991).



Study	Country	Environment	Dominant vegetation
Saarnio et al. (2013)	EU	Minerotrophic mires	
Hendriks et al. (2013)	NL	Floodplain Fen	*P. australis*
Schrier-Uijl et al. (2010b)	NL	Floodplain Fen	*P. australis*
Huth et al. (2013)	DE	Floodplain Fen	*P. australis*
Audet et al. (2013b)	DK	Floodplain Fen	*A.stolinifera*
Audet et al. (2013a)	DK	Floodplain Fen	*A. stolinifera*
Strumpshaw Fen	UK	Floodplain Fen	*P. australis*
Sutton Fen	UK	Floodplain Fen	*P. australis*

Figure 90 Comparison of ranges in annual CH_4 flux from Danish (DK), German (DE), Dutch (NL) and European (EU) lowland fens and Sutton and Strumpshaw Fens. Points represent mean values and bars denote minima and maxima values.

Observed peat temperatures used to parameterise the annual CH_4 reconstruction model were less than seasonal variation in peat temperature. Observed temperatures ranged from 2.2 to 17.3 ºC at Sutton Fen and 5.4 to 18.1 at Strumpshaw Fen, whilst seasonal variation in peat temperature reached a maximum of 27 ºC. This temperature difference may introduce a bias into the annual reconstructed CH_4 fluxes at higher temperature, especially as the model is sensitive to temperature (Figure 84).

There was great variance between the collar reconstructed annual CH_4 fluxes at both sites. These ranges are thought to be due to differences in plant species occurrence and abundance. At Sutton, collar two had the greatest reconstructed annual flux (27 g CH_4 m^{-2} yr^{-1}). This collar had the greatest abundance of *C. mariscus*, which is known to transport CH_4 through its aerenchyma (Chanton et al., 1993), at the site. *P. australis* was also present in the collar, which is another plant species that transports CH_4 actively and passively (Brix, 1989, Armstrong et al., 1992, Brix et al., 2001, Kaki et al., 2001). Similarly, collar 5 at Strumpshaw Fen had the highest reconstructed annual CH_4 flux at the site (24 g CH_4 m^{-2} yr^{-1}) and had a high abundance of *P. australis*, along with *E. cannabinum* and *G. palustre*.

6.6.2 CO_2-equivalent fluxes for Sutton and Strumpshaw Fen

GWPs over a 100-year period are generally used within the peatland literature to compare intra- and inter-site GHG exchange. At Sutton at Strumpshaw Fen it was anticipated that CH_4 emissions would be the greatest source of C to the atmosphere (H_9), due to the greater nutrient status of the site (section 3.3). CO_2-equivalent fluxes for CH_4 were significantly greater than CO_2 fluxes over a 20-, 100-, and 500- year horizon, resulting in H_9 being accepted. Despite annual CH_4 fluxes being less than CO_2 emissions on a molecule-per-molecule basis, CH_4 is a more potent GHG in the atmosphere than CO_2 (Forster et al., 2007). Thus it is necessary to reduce CH_4 emissions to the atmosphere to help reduce impacts on the greenhouse effect.

A difference in total C exchange (CO_2 + CH_4) over a 100-year period was investigated to establish which site was a greater overall sink of C. Strumpshaw Fen was a significantly greater C sink than Sutton Fen over a 20-, 100- and 500-year horizon, resulting in H_{10} being accepted. Strumpshaw Fen was anticipated as being the greatest C sink due to the greater nutrient status increasing aboveground green biomass and subsequently

CO_2 assimilation rates. Sutton Fen may have been a source of C between 1st September 2012 and 31st August 2013 due to the impacts of the two flood events at the site on the vegetation, with VGA being significantly less in 2013 compared to 2012. More research needs to be done to quantify C exchange within these sites to ascertain long-term trends and fluxes when vegetation is not significantly altered at only one site.

Annual terrestrial CO_2 and CH_4 fluxes over a 100 year period were within reported values in the literature (Table 60). Only Hendriks et al. (2007) has a full C flux (-86 g CO_2-equiv m^{-2} yr^{-1}) for lowland fens, which is significantly greater C uptake than Sutton Fen but not Strumpshaw Fen. The total C flux in Hendriks et al. (2007) includes CH_4 emission from ditches and ponds. When the aqueous CH_4 fluxes are omitted, the total C flux for the site is -297 g CO_2-equiv. m^{-2} yr^{-1}. Differences between Hendriks et al. (2007) and the two sites in this study may be caused due to flooding events in January and March 2013, as well as the relatively dry conditions during May to September 2013. The flood event in January and March 2013 altered vegetation dynamics at both sites and subsequently GPP. The alteration was especially pronounced at Sutton Fen, where VGA was less in 2013 than in 2012 (Figure 44). The summer of 2013 was especially dry, with rainfall less than the average for the 30 preceding years (Met Office, 2013). The lesser amounts of precipitation resulted in a low water level at both sites from June 2013 to September 2013 and a greater aerobic zone within the surface peat for heterotrophic respiration to occur.

6.6.3 Relative importance of fen and ditch CH_4 emissions

Observed CH_4 emissions reported in section 4.3 showed ditch fluxes to be significantly greater than fen fluxes and scaled fluxes according to surface area within both Sutton and Strumpshaw Fen were investigated.

6.6.3.1 Annual ditch CH_4 emissions

Contrary to the annual fen fluxes, a significant difference was observed between annual ditch fluxes between Sutton and Strumpshaw Fen (Table 57), with Sutton fen emitting more CH_4. Due to the small number of replicates for observed ditch CH_4 evasion rates, annual ditch fluxes may be biased and may not fully represent variation in evasion rates from ditches. Therefore, results from the annual ditch CH_4 emissions cannot be used to

calculate total C exchange but only in the scaled fluxes per surface area for ditches and fen.

The difference in annual ditch CH_4 evasion between the two sites was hypothesised to be due to differences in ditch nutrient concentrations (Figure 27 and 28, section 3.3.6), with significant differences in NO_3^-, SRP, SO_4^{2-} and Cl^- between sites (Table 18, section 3.3.6). Vermaat et al. (2011) suggested that the nutrient enrichment within ditches produce larger quantities of nutrient rich, readily decomposable organic matter that can be used by methanogens. This was not observed in this study, as Sutton Fen, the nutrient poorer site, has significantly greater evasion rates. In Vermaat et al. (2011), ditch fluxes were quantified in ditches from 14 different floodplain fens with dairy effluent inputs. Nutrient inputs into the ditches in Vermaat et al. (2011) were probably significantly greater than the riverine inputs observed in this study. No measurements of salinity are reported within Vermaat et al. (2011). It is thought that the smaller CH_4 evasion rates from Strumpshaw Fen are attributed the significantly greater Cl^- and SO_4^{2-} concentrations within the ditches (Table 18) as SO_4^{2-} has been shown to supress methanogenesis (Dise and Verry, 2001, Gauci et al., 2004, Gauci et al., 2005) and salinity reduces CH_4 solubility in water (Yamamoto et al., 1976).

Ditch 1 at Sutton Fen emitted the most CH_4 between 1st September 2012 and 31st August 2013. It is thought that the differences between the two ditches at Sutton are due to the ditch width. A small width, as in ditch 2, reduces wind speed due to the vegetation on the ditch banks, altering the agitation of the air-water boundary layer which controls evasion (Matthews et al., 2003). A greater ditch width will also reduce the shading of the ditch, causing an increase in temperature. Greater peat temperatures were observed in ditch 1 (2.6 to 23 °C) than in ditch 2 (1.8 to 18 °C) at Sutton Fen, potentially increasing microbial activity and methanogenesis. Ditch width was not incorporated into the reconstruction model as it was not a parameter that was quantitatively measured. However, understanding how ditch width can affect CH_4 evasion, ditch widths can be reduced to decrease CH_4 emissions to the atmosphere, whilst taking local fauna into account.

Table 60 Literature comparisons of CO_2 and CH_4 fluxes over a 100-year period. * is *Schoenoplectus tabernaemontani* (C.C.Gmel.) Palla 1888.

Study	g CO_2-equivalent m^{-2} yr^{-1}			Environment	Comments
	Total	NEE	CH_4		
Hendriks et al. (2007)	-86	-1141	223 621 114	Floodplain peat meadow under conservation management	Land Saturated land Water
Schrier-Uijl et al. (2010b)			459 ± 47 417 ± 17	Floodplain peat meadows	Intensive site Extensive site
Audet et al. (2013b)			-6.7 to 1278	Floodplain fen	
Billett et al. (2015)			463 ± 32 528 ± 30 1188 ± 125	Floodplain fen	*P. australis* *T. latifolia* *C. acutiformis*
Koch et al. (2014)			118 ± 70 3323 ± 438	Floodplain fen	*P. australis* Mixed veg.
Koebsch et al. (2013b)			35 90 ± 143 108 ± 30 143 ± 60	Floodplain fen	Site average *B. schoenus* *C. acutiformis* *S. tab**
Wilson et al. (2007b)		-1314 ± 339 -2237 ± 548 -1046 ± 449 -2297 ± 88 1031 ± 97		Lowland fen	*T. latifolia* *P. arundinacea* *Carex spp.* *Juncus spp.* Bare peat
Danevčič et al. (2010)			7.8 ± 0.25		*Arrhenatherum elatius*

Only one other study was found with an annual ditch CH_4 flux. In Van den Pol-van Dasselaar et al. (1999), annual fluxes ranged from 4.2 to 23 g CH_4 m^{-2} yr^{-1} in three floodplain fens in The Netherlands. The annual fluxes from Sutton and Strumpshaw fen are significantly greater than in Van den Pol-van Dasselaar et al. (1999). The difference between the two studies is thought to be due to the differences in pH between the sites. In Van den Pol-van Dasselaar et al. (1999), the three sites had a low pH (between 3.5 and 5.3), whilst at Sutton and Strumpshaw it was neutral (Figure 27E, section 3.3.6). pH is a controlling factor on methanogenesis (Table 33, section 4.3.6) and has been shown to inhibit methanogens (Le Mer and Roger, 2001), and could account for the greater fluxes at Sutton and Strumpshaw than within the Dutch study.

As for the annual fen fluxes, annual ditch fluxes for Sutton and Strumpshaw Fens showed a similar seasonal pattern to observed fluxes (Figure 51 and 87). As observed in other studies (Hendriks et al., 2007, Schrier-Uijl et al., 2010b), the seasonal pattern is due to temperature. Additionally, observed peat temperatures and barometric pressure used to parameterise the annual reconstruction model were less than seasonal variation in peat temperature and barometric pressure. Observed temperatures ranged from 2.6 to 17 ºC, whilst seasonal variation in peat temperature reached a maximum of 23 ºC and 18 ºC at Sutton Fen and Strumpshaw Fen, respectively. Observed barometric pressure ranged from 99.2 kPa to 102.9 kPa, whilst seasonal variation in peat temperature reached a maximum of 105.7 kPa and 105.6 kPa at Sutton Fen and Strumpshaw Fen. The temperature and barometric pressure difference may introduce a bias into the annual reconstructed CH_4 fluxes at higher temperatures and pressures, especially as the model is sensitive to temperature and barometric pressure (Figure 89).

6.6.3.2 Relative importance of fen and ditch emissions

Ditches at Sutton and Strumpshaw Fen emit significantly more CH_4 than the fen based on the sites based on upscaled annual fluxes (Table 59). At Sutton Fen, ditches emit 97 % of CH_4, despite only covering 4 % of the site. The remaining 3 % is emitted by the fen. At Strumpshaw Fen, the significantly lesser annual fluxes from Strumpshaw result in ditches emitting 80 % of the sites' CH_4 emissions. The ditches at Strumpshaw fen cover 21 % of the site, a greater area than Sutton due to the inclusion of two shallow ponds. The anoxic conditions within peat substrates below ditches due to the aquatic column above the peat and the lack of macrophytes oxidising the peat, promotes methanogenesis and CH_4 emissions via evasion (Schrier-Uijl et al., 2010a, Schrier-Uijl et al., 2010b). In addition, the specific heat capacity of water is greater than peat (Letts

et al., 2000), potentially resulting in ditches staying warmer for longer than the fen and subsequently increasing methanogenesis rates. Temperature also affects CH_4 solubility within water (Yamamoto et al., 1976), thus the longer periods of warmer temperature in the ditches than in the fen may result in greater CH_4 evasion.

The relative importance of the ditches as CH_4 sources are significantly greater than those reported in the literature (Hendriks et al., 2007), with aquatic (ditch) and terrestrial (fen) CH_4 emission measured in in a floodplain grassland on peat in The Netherlands. In the Dutch study, ditches emitted 25 % of the CH_4 from the site in both 2005 and 2006, despite covering only 10 % of the surface area (Hendriks et al., 2007). A greater annual terrestrial CH_4 flux (43 g CH_4 m^{-2} yr^{-1}) and smaller annual aquatic flux (11 G CH_4 m^{-2} yr^{-1}) in Hendriks et al. (2007) than at Sutton and Strumpshaw Fen (Table 59) cause the difference in scaled fluxes. Differences in substrate may explain differences in CH_4 emissions, as in Hendriks et al. (2007), the substrate is a mix of peat, clay and sand through the profile. At Sutton and Strumpshaw fens, the substrate is only made up of peat throughout the profile (section 3.3.1), possibly resulting in greater methanogenesis throughout the entire peat profile due to better substrate quality.

The relative importance of the fen and ditches at both sites may overestimate the contribution of each terrestrial and aquatic environment. Error associated with the parameterisation of the ditch model may contribute to error in annual ditch fluxes. Additionally, the small number of replicates for ditch fluxes will contribute to annual flux estimate errors. The upscaling method may too add to errors in the relative importance of each environment. However, an estimate for the relative contribution of each environment was desired to generally compare the two environments. A more in depth study into both fen and ditch CH_4 emission, with a greater number of replicates, is necessary to better quantify the relative importance of ditch and fen CH_4 emission.

6.7 Summary and synthesis

This chapter sought to quantify annual CO_2 exchange (R_{eco}, GPP and NEE) and CH_4 emissions between two floodplain fen sites of differing nutrient status (R.Q.5) and to ascertain CO_2-equivalent GHG fluxes for the two floodplain fen sites (R.Q.6), with the aim of establishing if the sites were a net sink or source of C. Annual R_{eco} and GPP were significantly greater at Strumpshaw Fen, the more nutrient enriched site (section 3.3), than at Sutton fen; however, no significant difference was observed for annual fen CH_4 emissions, resulting in H_8 only being partially accepted. Differences in VGA and nutrient status between the two sites are attributed to the greater annual CO_2 fluxes. The lack in difference in annual CH_4 emissions between sites is also attributed to the VGA and porewater chemistry. Annual ditch CH_4 fluxes were shown to be significantly different between sites, as well as being significantly greater than annual fen CH_4 fluxes when scaled to surface area.

CH_4 fluxes were found to be significantly greater than CO_2 exchange at both sites based on CO_2-equivalent data, resulting in H_9 being accepted. The high water levels at the two sites for the majority of the sampling period promoted anoxic conditions within the peat substrate and subsequently methanogenesis. Strumpshaw Fen was found to be a significantly greater C sink than Sutton Fen, resulting in H_{10} being accepted. The greater nutrient status at Strumpshaw Fen than at Sutton Fen promoted vegetation growth, leading to a significantly greater aboveground green biomass and VGA to sequester CO_2. High water levels throughout the majority of the sampling period also helped to reduce R_{eco}. Knowing how water levels affect vegetation dynamics and C exchange in floodplain fens, sites can be managed accordingly. Maintaining a water level around the peat surface will minimise CO_2 emissions from the fen and allow emissions to be offset by CO_2 sequestration rates by vegetation. Encouraging flood waters to flow out of floodplain fens as quickly as possible will help to minimise CH_4 emissions and negative impacts on vegetation dynamics, especially if flooding occurs around the beginning of the growing season, as observed at Sutton Fen. Nutrients also have a significant effect on C dynamics in floodplain fens; however, the impact of individual macronutrients are hard to elucidate *in situ*. The ratio of ditch to fen surface area needs to be carefully considered in floodplain fens to help minimise CH_4 emissions. This study showed the importance of ditches as a CH_4 source to the atmosphere with the scaled fluxes in section 6.5.

7. Potential greenhouse gas production

This chapter presents data from a laboratory-based fertilisation study to ascertain impacts of short-term nutrient pulses on potential greenhouse gas (GHG) production within floodplain fen peat (R.Q. 7). Previous chapters demonstrated the difference in CO_2 and CH_4 exchange (chapter 4) from floodplain fens of different nutrient status. A significant difference in annual reconstructed ecosystem respiration (R_{eco}), gross primary productivity (GPP) and net ecosystem respiration (NEE) was observed in chapter 6. Differences in R_{eco}, GPP and NEE were caused due to differences in nutrient status (section 3.3), with soluble reactive phosphorous (SRP) and NO_3^- acting as controlling factors (section 4.3.6). A significant difference was not observed in annual CH_4 emissions between sites (section 5.4), but SRP and NO_3^- were still shown to be controlling factors on CH_4 emission (section 4.3.6). Elucidating the factors responsible for GHG production under field conditions is extremely difficult, thus necessitating a controlled laboratory experiment. The impacts of nutrient loading via fluvial inundation on GHG emission are not well known. Rivers in agricultural catchments have the potential to pollute floodplain fens with significant concentrations of nutrients, such as nitrogen (N) and phosphorous (P). Under UK and EU flooding policies, lowland environments such as floodplain fens can be inundated with floodwaters to mitigate urban flooding (Defra, 2005, Lamers et al., 2006, Acreman and Holden, 2013), increasing the probability of such environments being flooded with nutrient rich water. Whereas other authors (Aerts, 1997a, Aerts and Toet, 1997, Amador and Jones, 1997, Aerts and de Caluwe, 1999, Lund et al., 2009a, Deyan and Changchun, 2010) have studied the effects of nutrient loading under aerobic conditions associated with atmospheric deposition (section 7.1), the effects of inundation with N and P on GHG emissions under anaerobic conditions have not been researched to date and are not well understood. The following research question and hypotheses (H) will be answered within this chapter:

R.Q.7. How does potential production of CO_2, CH_4 and N_2O change with fertilisation of N and P loads in nutrient-rich and nutrient-poor floodplain fen peat?

H_{11}: Potential CO_2, CH_4 and N_2O production will be greater in nutrient-rich than in nutrient-poor peat.

The initial higher concentrations of N and P in the substrate will mean that there will be a greater microbial biomass (measured using substrate-induced respiration method at the start and end of experiment) and C and N will be mineralised at a faster rate.

H_{12}: NPG fertilisation will increase potential CO_2 and N_2O production rates more than other treatments.

An increase in available nutrients will increase available reactants, such as NO_3^- and PO_4^{3-}, for respiration and denitrification, as seen in Aerts (1997a), Aerts and de Caulwe (1999) and D'Angelo and Reddy (1999). With N and P being limiting in microbial processes (Basiliko et al., 2007), fertilisation with both macronutrients will facilitate greater mineralisation rates.

H_{13}: PG fertilisation will increase potential CH_4 production rates more than other treatments the most.

Microbes are often P limited (Basiliko et al., 2007), hence the addition of PO_4^{3-} will increase methanogenesis, as seen in Aerts and de Caluwe (1999). NO_3^- is known to supress methanogenesis as it is a non-specific methanogenic inhibitor (Roy and Conrad, 1999, Smemo and Yavitt, 2011). Studies by Watson and Nedwell (1998), Nykanen et al. (2003) and Liu and Greaver (2009) have shown a reduction in CH_4 emissions with NO_3^- addition.

Firstly, an introduction to current understanding of N and P fertilisation studies is given in section 7.1 (see section 2.3.1 for a description of carbon (C) and N cycles). The microcosm methodology is then presented in section 7.2, outlining the experimental approach (section 7.2.1), sample collection (section 7.2.2), laboratory methods (section 7.2.3 – 7.2.7) and post-experiment analysis (section 7.2.8). Results from the experiment are presented in section 7.3, reporting potential GHG production and fluxes from different treatments (section 7.3.1), microbial biomass alterations (section 7.3.2) and changes in microbial activity (section 7.3.3). Section 7.4 discusses the results and contextualises them within the perspective of flooding of floodplain fens with nutrient-rich water. Finally, section 7.5 summarises and synthesises the findings.

7.1 Peat fertilisation studies with N and P

Previous studies have focused on the effects of N and P fertilisation under oxic conditions, to simulate atmospheric nutrient deposition. Aerts (1997a) found that additions of NO_3^- significantly increased N_2O production via denitrification in peat from a Dutch floodplain fen, whilst NH_4^+ did not induce a significant increase in N_2O production. Aerts (1997a) attributed the lack of N_2O production to a lack of nitrifiers in the substrate

to convert NH_4^+ into NO_3^- prior to denitrification. Deyan and Changchun (2010) found that both N and P additions significantly increased potential N_2O production in a floodplain marshland sediment, due to the stimulation and proliferation of denitrifiers. Aerts and de Caluwe (1999) found that fertilisation with NH_4^+ had a negative impact on CO_2 emissions due to the acidification of the floodplain fen peat, whilst PO_4^{3-} additions increased emissions in low nutrient sites due to the supply of reactants. Furthermore, the supply of reactants to peat increased net CH_4 emissions, due to the proliferation of the microbial biomass and an increase in microbial activity, as well as NH_4^+ reducing CH_4 oxidation (Aerts and de Caluwe, 1999). Watson and Nedwell (1998) simulated NO_3^- deposition on ombrotrophic peat in a laboratory-based study and found that 6.2 mg L^{-1} NO_3^- significantly decreased CH_4 formation. The authors did not suggest a mechanism for the reduction in methanogenesis but other studies have shown that high NO_3^- inputs can inhibit methanogens either by changing the C:N ratio within the substrate and inducing C immobilisation or NO_3^- has been shown to be toxic to methanogenic archaea (Smemo and Yavitt, 2011). However, fertilisation of peat microcosms with 0.3, 0.6 and 3.1 mg L^{-1} NO_3^- had no statistically significant effect on CH_4 formation rates (Watson and Nedwell, 1998).

It is necessary to establish how N and P additions would alter potential GHG production under anaerobic conditions as the dominant mineralisation processes are different under anaerobic conditions. Heterotrophic respiration will be significantly reduced due to a lack of oxygen under anaerobic conditions; instead, fermentation will become the dominant process in CO_2 production, which is a much slower process than heterotrophic respiration in aerobic conditions. Anaerobic conditions will promote methanogenesis, an anaerobic process, whilst methanotrophy will be reduced as methanotrophic bacteria are strict aerobes, resulting in greater rates of CH_4 emission than under aerobic conditions or at the boundary between the two (Segers, 1998). N_2O production is expected to be via denitrification rather than nitrifier denitrification, which is an aerobic process.

The objective of this chapter is to ascertain changes in potential production of CO_2, CH_4 and N_2O with fertilisation of nutrient-rich and nutrient-poor floodplain fen peat by the addition of NO_3^- and SRP (R.Q. 7). Undertaking potential GHG production experiments under anaerobic conditions allows the elucidation of alterations to rates of fermentation, methanogenesis and denitrification, and to compare the results between different sites more easily than an ecosystem-based study. Floodplain fens provide an excellent environment to undertake such research due to their lowland location and inundation

during high river flows. These environments are saturated and anoxic for a large part of a year, such as at Sutton Fen and Strumpshaw Fen (Figure 32), which were saturated for approximately 80 % of the year.

7.2 Laboratory experiment methodology

7.2.1 Laboratory experiment approach

To measure potential GHG production, an *ex situ* microcosm study was chosen. This approach allows the exploration of purely microbial dynamics, unlike a whole ecosystem approach, which makes the elucidation of alterations to microbial dynamics difficult due to the inherent complexity of the natural system. Additionally, an *in situ* study was not feasible for this research due to time constraints. Long-term alterations to C cycling from fertilisation studies have already been researched (Keller et al., 2005, Eriksson et al., 2010). This study was, however, only focused on short-term alterations (1 to 15 days, rather than > 15 days) to GHG production, as this should help identify potential changes to GHG production dynamics during a nutrient pulse from fluvial inundation.

A pilot study showed peat to be labile C limited (Appendix 6), thus it was decided to fertilise samples with glucose (G). This C source was chosen as it is a simple labile C source and is readily metabolised by r-strategist microbes (Shackle et al., 2000). The processes involved in the transformation of glucose to CO_2 or acetate and then methane are presented in section 2.3.1.1. When a site is flooded with nutrient rich water, it is the r-strategist microbes that proliferate on labile organic C (Ryan, 1991). In river water, labile organic C occurs in the form of dissolved organic C (DOC; concentrations ranged between 0 and 56 mg L^{-1} DOC for the rivers Ant and Yare between June 2012 and September 2013; Figure 3.19) that will provide most of the short-term alterations to GHG emission derived from microbes. DOC was found to be a significant controlling factor on R_{eco} and CH_4 emissions (Table 33, section 4.3.6). Hence it was necessary to ensure that this population was active for the experiment. A fully factorial design was used to ascertain alterations to potential GHG production, including a control (Co), G (glucose addition), NO_3^- + G (NG), PO_4^{3-} + G (PG) and NO_3^- + PO_4^{3-} + G (NPG) treatment for both nutrient-poor and nutrient-rich floodplain fen peat. Sutton Fen provided the substrate for the nutrient-poor peat and the nutrient-rich peat came from Strumpshaw Fen (section 3.1). Samples were taken from within the same sampling areas for the field based study (R.Q. 1 to 2; Figure 8 and 9). All treatments were analysed in septuplicate.

7.2.2 Sample collection

Peat samples were taken from within the area delineated by the field campaign under research questions 1-4 (areas cut in 2009; section 3.1). 30 surface peat samples were taken from each site from only the top 0 - 10 cm depth (Amador and Jones, 1993), by cutting the peat with a serrated knife and removing the whole intact peat sample. Surface peat is likely to be the most sensitive to nutrient and C additions as it will initially receive most of the floodwater with inundation and it is the zone where most oxic-anoxic interactions occur. In addition, surface peat is where there is a large proportion of roots and rhizomes, which can provide labile C in the form of root exudate for heterotrophic respiration, methanogenesis and denitrification. One litre samples were taken randomly from within the delineated area for the field campaign (R.Q. 1- 4), as to reduce any bias in selection and to get a representative sample from both sites. Samples were double bagged in sealable polythene sample bags to reduce oxygen diffusion into the sample. Once collected, samples were put on ice until processing.

7.2.3 Sample processing

In the laboratory, samples were processed in an anaerobic hood to retain anaerobic conditions and samples were pooled together to reduce heterogeneity. Roots and rhizomes were removed to prevent a C pulse via mineralisation at the start of the experiment (Deyan and Changchun, 2010) by passing the peat through a 0.2 mm fine sieve and the peat was then homogenised by stirring gently to ensure good mixing of microbial populations (Amador and Jones, 1993).

A sub-sample was removed and oven dried at 70 ºC until a constant weight to calculate moisture content, using the following calculation:

$$W = \frac{(M_{wet} - M_{dry})}{M_{dry}} \cdot 100 \qquad \text{Eq. 24}$$

where *W* is the water content by mass (%), M_{wet} is the mass of wet sediment (g) and M_{dry} is the mass of dry sediment (g).

Wet mass of 1 $g_{dry\ weight}$ was then calculated using following calculation:

$$\frac{M_{wet}}{M_{dry}} = 1 + \frac{W_M}{100} \qquad \text{Eq. 25}$$

where $\frac{M_{wet}}{M_{dry}}$ is the g wet mass per g of dry sediment, W_M is the average water content (%) by mass.

Fully homogenised peat, 2.4 and 2.8 g of wet weight corresponding to 2 g dry weight for Sutton and Strumpshaw fen peat, respectively, was placed in a 50 ml serum bottle. 2 ml of ultrapure water (UHQ) degassed with oxygen-free nitrogen (OFN) was added to make a slurry as in Dierberg et al. (2011) and the serum bottles were sealed with a gas impermeable butyl rubber septa as in Blazewicz et al. (2012). Any excess peat was kept refrigerated. Once the serum bottle was sealed, the headspace was flushed with oxygen-free nitrogen (OFN) for 20 minutes. The substrate was left to equilibrate for 3 days, to ensure that all oxygen was depleted as in Smemo and Yavitt (2007), in an incubator at 16 °C (based on surface peat temperatures from the two sites, see Figure 91).

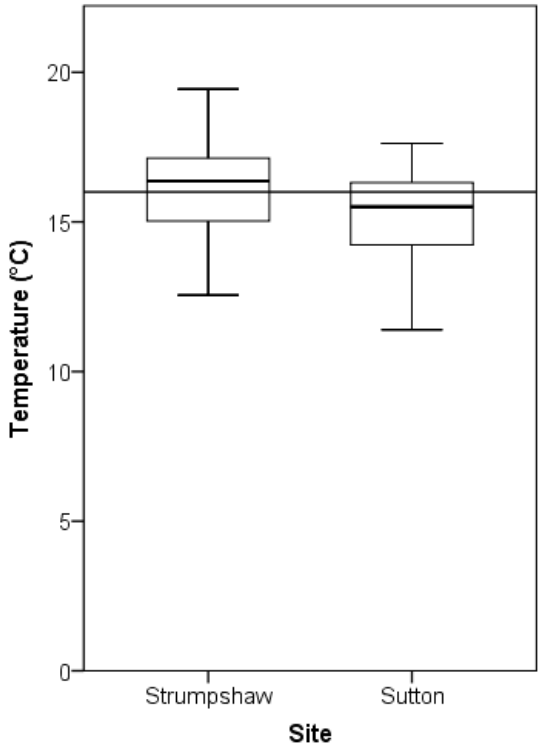


Figure 91 Average hourly summer surface peat temperatures for June 2012 to August 2012. Boxes represent the interquartile range and the thick horizontal lines indicate the group mean. Bottom whiskers represent values in the lower quartile, while top whiskers represent those in the upper quartile. The horizontal line represents the average temperature between both sites.

Fertilisation solutions were prepared to give final concentrations of 51 mg L^{-1} NO_3^--N, 1.4 mg L^{-1} PO_4^{3-}-P and 1000 mg L^{-1} $C_6H_{12}O_6$, using $NaNO_3$, NaN_2PO_4 and $C_6H_{12}O_6$ in UHQ. These concentrations were chosen as they represent a threefold increase in maximum observed river water NO_3^- and SRP concentrations (Figure 30, section 3.3.6). All concentrations were chosen to be in excess, based on other studies. Fertilisation solutions were deoxygenated using OFN for 20 minutes (D'Angelo and Reddy, 1999) as to retain anaerobic conditions within the serum bottles and solutions were stored in OFN flushed serum bottles.

7.2.4 Sample incubation

After the equilibration period, slurry-filled serum bottles were shaken vigorously to ensure no bubble accumulation within the slurry, then flushed with OFN for 10 minutes and shaken again. A 0.6 mL gas headspace was taken (T = 0 hours) and injected into a 3 mL exetainer filled with a deoxygenated (with OFN) saline solution (58 mg L^{-1}), allowing the excess 0.6 mL solution to flow out through a secondary needle. A saline solution was used to prevent any microbial activity from occurring if any peat was introduced into the exetainer accidentally and to prevent gas diffusing into the aqueous medium (Preuss et al., 2013).

Samples were then fertilised with their required solutions, shaken and returned to the incubator. The control samples had deoxygenated UHQ added instead of a fertilisation solution. Another sample was taken at T = 1 hour for control and fertilised samples, shaken before a headspace sample was taken. Samples were then re analysed every 24 hours for 7 days and then every 48 hours thereafter until 15 days (at 24, 48, 72, 96, 120, 144, 192, 240 and 366 hours).

7.2.5 Sample Analysis

Gas samples were analysed using the same method as the field based study (outlined in section 4.2.3). Briefly, a 7 point calibration curve was created by diluting gas mix (Scientific and Technical Gases Ltd – 98.8 ppm N_2O, 98.7 ppm CH_4 and 3706 ppm CO_2) and 100% CO_2 and CH_4 with OFN. Drift samples were made up in the same way to calibration standards to check for short-term analytical drift and are shown in Table 49.

Results were rejected and reanalysed if drift was > 10%. CO_2, CH_4 and N_2O fluxes were calculated from linear increases in concentration over time.

Table 61 GC average RSD (%) for short-term analytical drift

Gas (concentration in ppm)	Average RSD (%)
CO_2 (61.78 ppm)	5.9
CH_4 (1.6 ppm)	6.9
N_2O (0.33 ppm)	6.0

7.2.6 Microbial activity

Total microbial activity was quantified both pre- and post-experiment in triplicate using the fluorescein diacetate (FDA) method (Adam and Duncan, 2001, Pesaro et al., 2004, Sánchez-Monedero et al., 2008). This method was chosen as it is an accurate, sensitive and simple method to quantify total microbial activity. Additionally it is a widely accepted method for total microbial activity in soils (Schnürer and Rosswall, 1982, Adam and Duncan, 2001).

The FDA method works by using fluorescein conjugated two acetate radicals (FDA), which is a colourless compound (Adam and Duncan, 2001). When the FDA is added to a substrate, such as peat, it is hydrolysed by both free (exoenzymes) and membrane bound enzymes, releasing the fluorescein within the compound (Adam and Duncan, 2001). Fluorescein is a coloured end product that absorbs strongly in the visible wavelength of 490 nm, enabling it to be measured on a spectrophotometer (Adam and Duncan, 2001). The more enzymic activity, the more FDA hydrolysised and the stronger the fluorescein colour.

Peat (1 $g_{dry\ weight}$) was weighed into a 12 mL solvent resistant centrifuge tube (Fisher Scientific). For each treatment, three control and three fertilised samples were used. All samples had 3 mL of phosphate buffer added and then fertilised samples had 0.1 mL of FDA added (Adam and Duncan, 2001). The time was noted and then samples shaken until the sample changed colour. 3 mL of acetone was then added to stop the reaction and the time noted. Samples were then centrifuged and the supernant analysed on the spectrophotometer at 490 nm (Adam and Duncan, 2001).

A calibration series was created using fluorescein salt (Fisher Scientific). A 2000 µg fluorescein mL^{-1} stock solution was made using fluorescin sodium salt and 50:50 phosphate buffer:acetone (Adam and Duncan, 2001). The calibration range was made up by diluting down the stock using 50:50 phosphate buffer:acetone. The calibration series was used to ascertain the molar absorbance, using Beer's law:

$$A = \in \cdot l \cdot c \qquad \text{Eq. 26}$$

where A is the absorbance measured on the spectrophotometer at 490 nm, $\in$ is the molar absorptivity coefficient (µM cm^{-1}), l is the cell path length (cm) and c is the concentration of FDA (µmol L^{-1}). Absorbance of a sample due to the presence of fluorescein, ABS_{490} was calculated as measured absorbance of the treatment sample, *A*, minus absorbance of the blank solution and of the control.

The rate of FDA hydrolysis was calculated as:

$$R_{FDA} = \frac{ABS_{490}}{\in} \cdot \frac{V_a}{M_d} \cdot \frac{1}{T} \qquad \text{Eq. 27}$$

Where R_{FDA} is the rate of FDA hydrolysis (µmol $g^{-1}_{\text{dry sediment}}$ min^{-1}), V_a is the volume of the assay (mL), M_d is the mass of dry sediment (g) and T is the amount of time between the addition of FDA and termination of the reaction by the addition of acetone (min).

7.2.7 Microbial biomass

Microbial biomass was measured both pre- and post-experiment to ascertain if alteration occurs with addition of nutrients and differences between sites. The biomass was ascertained using the substrate induced respiration (SIR) method, whereby peat was subject to fertilisation using glucose in excess (Anderson and Domsch, 1978, Wright and Reddy, 2007). SIR was chosen as the method to ascertain microbial biomass as it only measures active biomass, whereas methods such as chloroform fumigation extraction measures total biomass (Anderson and Domsch, 1978, Bailey et al., 2002). Only the quantification of the active portion of the biomass was wanted as this would be the population mineralising OM. Other advantages to SIR include the rapidity and flexibility of the method, low cost and requirement for small quantities of sample (Sparling, 1995).

Pre-experiment SIR samples were processed as described in sections 7.2.2 to 7.2.3. Samples were oxygenated[4] prior to placing 2 $g_{dry\ weight}$ peat into a 12 mL exetainer. For both sites, triplicate control and fertilised samples (n = 6) were prepared. A 1 g L^{-1} glucose solution was prepared in UHQ and 1 mL was added to the fertilised samples before sealing the exetainers with a butyl rubber septa and PVC lid. Samples were analysed over 30 hours using GC-FID (method explained in section 4.2.3) (Bailey et al., 2002, Preston et al., 2012).

Microcosm experiment samples were used for post- experiment SIR samples, with each microcosm treatment being analysed for microbial biomass. Three samples from each treatment were divided into 12 mL exetainers (n = 6 per treatment) for a control and a fertilised sample, noting the weight of the sample as to calculate the substrate dry weight. Control and fertilised samples had UHQ and glucose solution added, respectively, as described for the pre-experiment samples and were analysed over 30 hours.

SIR data was expressed as concentrations of CO_2 over time allowing inter-site comparisons. Data was transformed into microbial C biomass using a standard equation used in the literature from Anderson and Domsch (1978):

$$x = 40.04 \cdot y + 0.37 \qquad \text{Eq. 28}$$

where x is the total microbial C biomass (mg microbial C $g^{-1}_{dry\ weight}$), 40.04 is the microbial biomass coefficient and y is the greatest initial rate of CO_2 respiration (mL CO_2 $g^{-1}_{dry\ weight\ sediment}$).

7.2.8 Statistical analysis

All statistical work was carried out in R version 3.1.1 (R Core Team, 2014). The Bunsen coefficient was used to account for CH_4 (Yamamoto et al., 1976), CO_2 (Weiss, 1974) and N_2O (Weiss and Price, 1980) in aqueous solutions in the peat slurries and water-filled 3 mL exetainers, taking salinity into account. Potential CH_4 and N_2O production rates were calculated by linear regression over time as in D'Angelo and Reddy (1999). Potential CO_2 production rates were calculated using non-linear regression due to the response

[4] During the pilot study an anaerobic SIR method was trialed but was not successful, hence the aerobic method was chosen. There is the potential for anaerobic microbial biomass not to be properly quantified using this method; however, there are no other methods to quantify active microbial biomass.

of CO_2 under anaerobic conditions. A CO_2 flux was calculated from 96 hours onwards. Potential production rates were then compared between treatments using ANCOVA, with time as the covariate. A one-way ANOVA was used to determine the difference in potential production between sites.

7.3 Results

7.3.1 Potential GHG fluxes

CO_2 production is shown in Figure 92. Fluxes were generally similar between sites, with no clear difference between the two sites. Higher starting concentrations in samples fertilised with G, including NG and PG, were observed. Additionally, no steady increase in concentration over time was observed. A drop in concentration at 96 hours was, however, observed for all but the PG samples at Strumpshaw. A gradual non-linear increase in concentration was then observed from 96 hours. Potential CO_2 fluxes were calculated using data from 96 to 336 hours (Table 62). CO_2 fluxes also showed significant differences between treatments ($F_{4,419}$ = 11.844 $p < 0.001$), time ($F_{1,419}$ = 95.038, $p < 0.001$) and site ($F_{1,149}$ = 5.721, $p = 0.017$) from 96 hours to the end of the experiment. No significant interactions between factors were observed ($F_{4,419}$ = 1.281, $p = 0.276$).

Converse to CO_2 production, a difference between sites was observed in CH_4 production (Figure 93). Peat from Strumpshaw Fen generally had greater CH_4 fluxes than peat from Sutton Fen (Table 62). All fluxes were significantly greater at Strumpshaw than Sutton, apart from the control (Table 62). ANCOVA (between factors: treatment and site; covariate: time) showed CH_4 production was significantly different between treatments ($F_{4,120}$ = 15.026, $p < 0.001$), site ($F_{1,120}$= 38.646, $p < 0.01$) and time ($F_{9,120}$ = 148.341, $p < 0.001$). No significant interaction between factors was observed ($F_{4,120}$ = 2.433, $p = 0.052$). A difference in the pattern of potential production was also noted for CH_4, with concentrations steadily increasing until around 144 hours for Sutton Fen and 288 hours for Strumpshaw Fen. A decrease in CH_4 production was noted in Sutton Fen samples only, indicating either CH_4 uptake or removal. The increase in CH_4 production does not follow the same pattern in the control samples. The concentrations in the control samples increase steadily until 144 hours where there is a sudden increase in CH_4 production. From 24 hours to 144 hours, Sutton has a greater average flux (0.07 ± 0.05 nmol $g^{-1}_{dry\ weight}$ h^{-1}) than Strumpshaw Fen (0.03 ± 0.001 nmol $g^{-1}_{dry\ weight}$ h^{-1}). After 144 hours the pattern switches and Strumpshaw has a significantly greater potential flux (0.71 ± 0.04 nmol $g^{-1}_{dry\ weight}$ h^{-1}) than Sutton (0.1 ± 0.03 nmol $g^{-1}_{dry\ weight}$ h^{-1}) in the control samples

(Table 62). Samples fertilised with PG had the highest potential CH_4 production for both Sutton (144 hours) and Strumpshaw Fen (336 hours) and the highest potential fluxes (3.9 ± 0.43 and 6.6 ± 0.18 nmol $g^{-1}_{dry\ weight}$ h^{-1}, for Sutton and Strumpshaw, respectively). Samples fertilised with G had the second highest potential flux (3.7 ± 0.43 and 6.3 ± 0.09 nmol $g^{-1}_{dry\ weight}$ h^{-1}). Samples fertilised with NO_3^- (N and NPG) had lesser CH_4 production than samples fertilised without NO_3^- (G and PG).

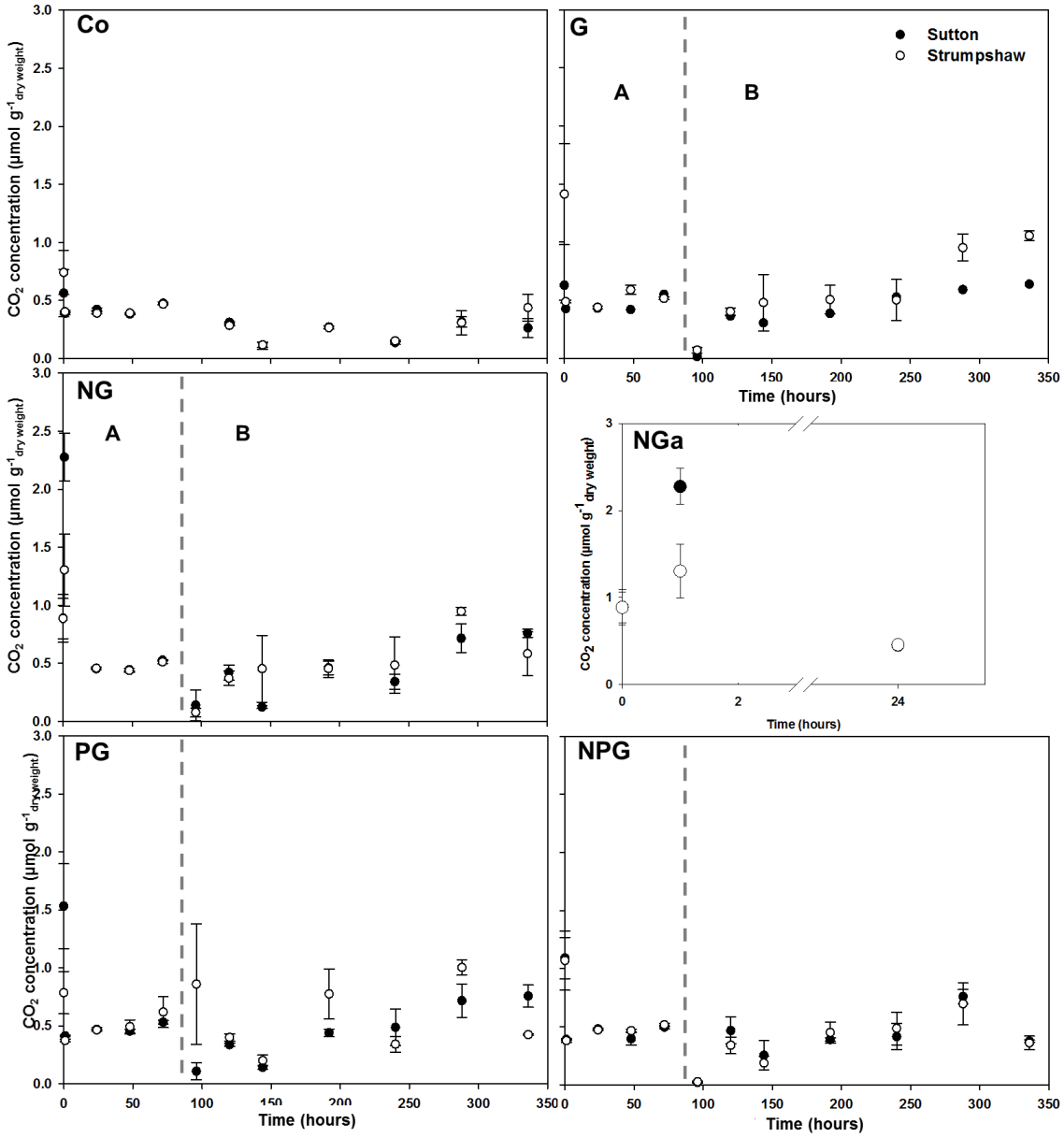


Figure 92 Potential CO_2 production for control (Co), glucose (G), nitrate + glucose (NG) and insert (NGa; NG fertilised sample CO_2 concentrations until 24 hours), phosphate + glucose (PG) and nitrate + phosphate + glucose NPG treatments for nutrient-poor (Sutton Fen) and nutrient-rich (Strumpshaw Fen) peat. Section A represents an increase in CO_2 concentration before a sudden decrease between 72 and 96 hours and a second increase in CO_2 concentration in section B. Points represent mean values and error bars denote ± 1 standard error.

Table 62 Potential CO_2, CH_4 and N_2O fluxes for each treatment (Co = control, G = Glucose, NG = nitrate and glucose, PG = phosphate and glucose and NPG = nitrate, phosphate and glucose) for nutrient-poor (Su = Sutton) and nutrient-rich (St = Strumpshaw) sites.

Treatment	Site	Flux			
		CO_2 (nmol $g^{-1}_{dry\ weight}$ h^{-1})	CH_4 (nmol $g^{-1}_{dry\ weight}$ h^{-1})		N_2O (nmol $g^{-1}_{dry\ weight}$ h^{-1})
			< 150 hours	> 150 hours	
Co	Su	1.5 [± 0.44]	0.07 [± 0.05]	0.10 [± 0.03]	-0.09 [± 0.03]
	St	2.4 [± 0.60]	0.03 [± 0.001]	0.71 [± 0.04]	-0.13 [± 0.04]
G	Su	3.3 [± 0.78]	3.7 [± 0.43]	-0.53 [± 0.10]	-0.16 [± 0.02]
	St	5.1 [± 0.21]	6.3 [± 0.09]		-0.08 [± 0.05]
NG	Su	3.2 [± 0.72]	3.7 [± 0.16]	-0.19 [± 0.01]	0.57 [± 0.06]
	St	2.6 [± 0.91]	4.9 [± 0.2]		0.25 [± 0.08]
PG	Su	3.4 [± 0.79]	3.9 [± 0.43]	-0.88 [± 0.27]	-0.04 [± 0.03]
	St	1.4 [± 0.32]	6.6 [± 0.18]		-0.09 [± 0.02]
NPG	Su	1.9 [± 0.05]	3.1 [± 0.22]	-0.21 [± 0.08]	0.70 [± 0.03]
	St	1.7 [± 0.29]	5.0 [± 0.08]		0.36 [± 0.02]

N_2O production occurred very quickly after fertilisation (Figure 94). N treatments (NG and NPG) increased in concentration from 0 hours to 1 hour and then decreased again. Slightly greater concentrations were observed for the NPG treatments than NG but differences were not statistically significant. N_2O production (Table 62) was significantly greater for Sutton than Strumpshaw for both NG and NPG treatments (t_{12}= 6.539, p < 0.001 and t_{12}= 7.273, p < 0.001, respectively). Non-N treatments showed a decrease in concentration from 0 to 96 hours.

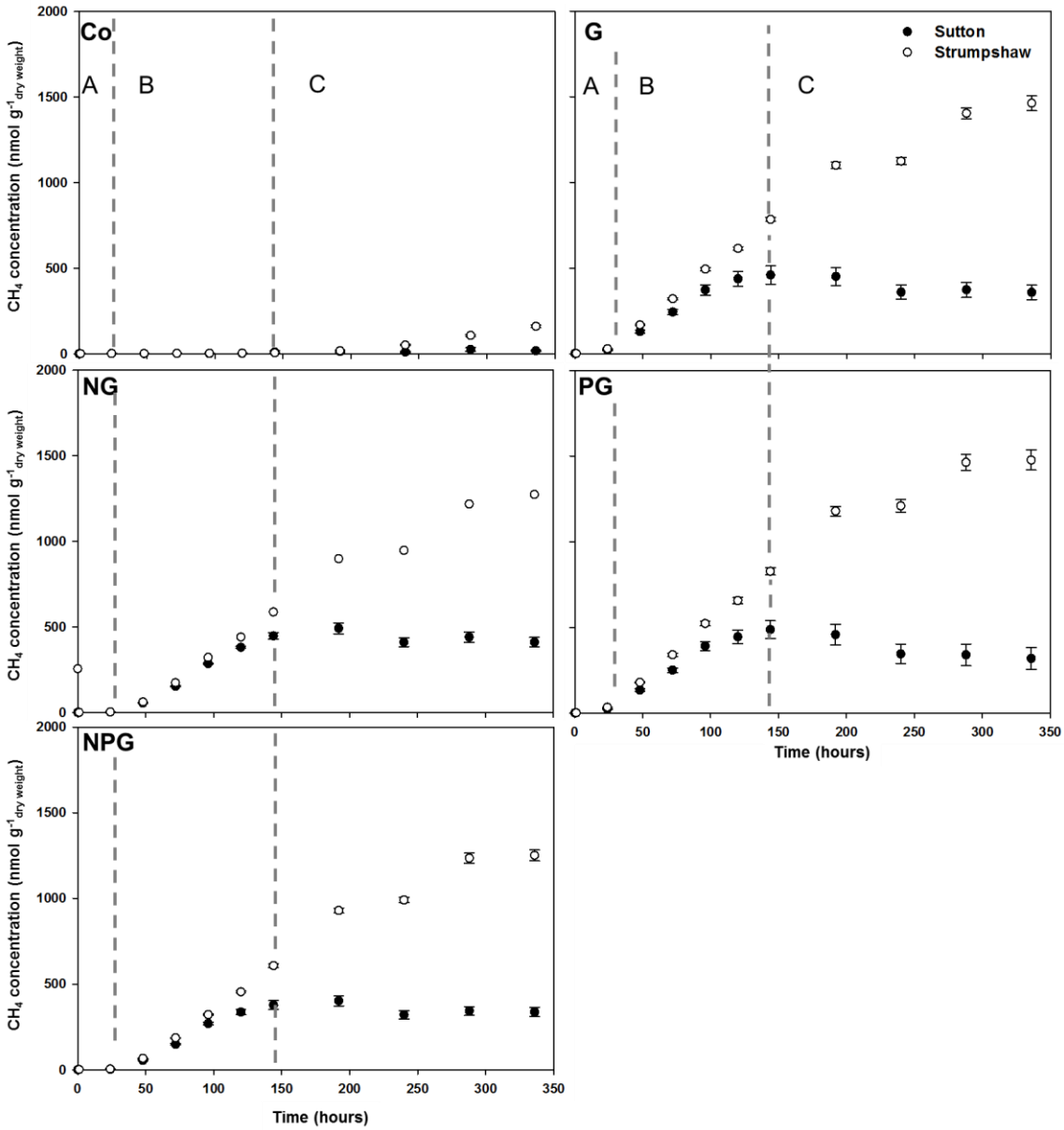


Figure 93 Potential CH_4 production for control (Co), glucose (G), nitrate + glucose (NG), phosphate + glucose (PG) and nitrate + phosphate + glucose NPG treatments for nutrient-poor (Sutton Fen) and nutrient-rich (Strumpshaw Fen) peat. Other mineralisation processes dominate during section A (0 to 24 hours), before an increase in CH_4 occurred from 24 hours onwards (B) followed by a reduction in CH_4 concentration in Sutton fen samples from 144 hours (C). Points represent mean values and error bars denote ± 1 standard error.

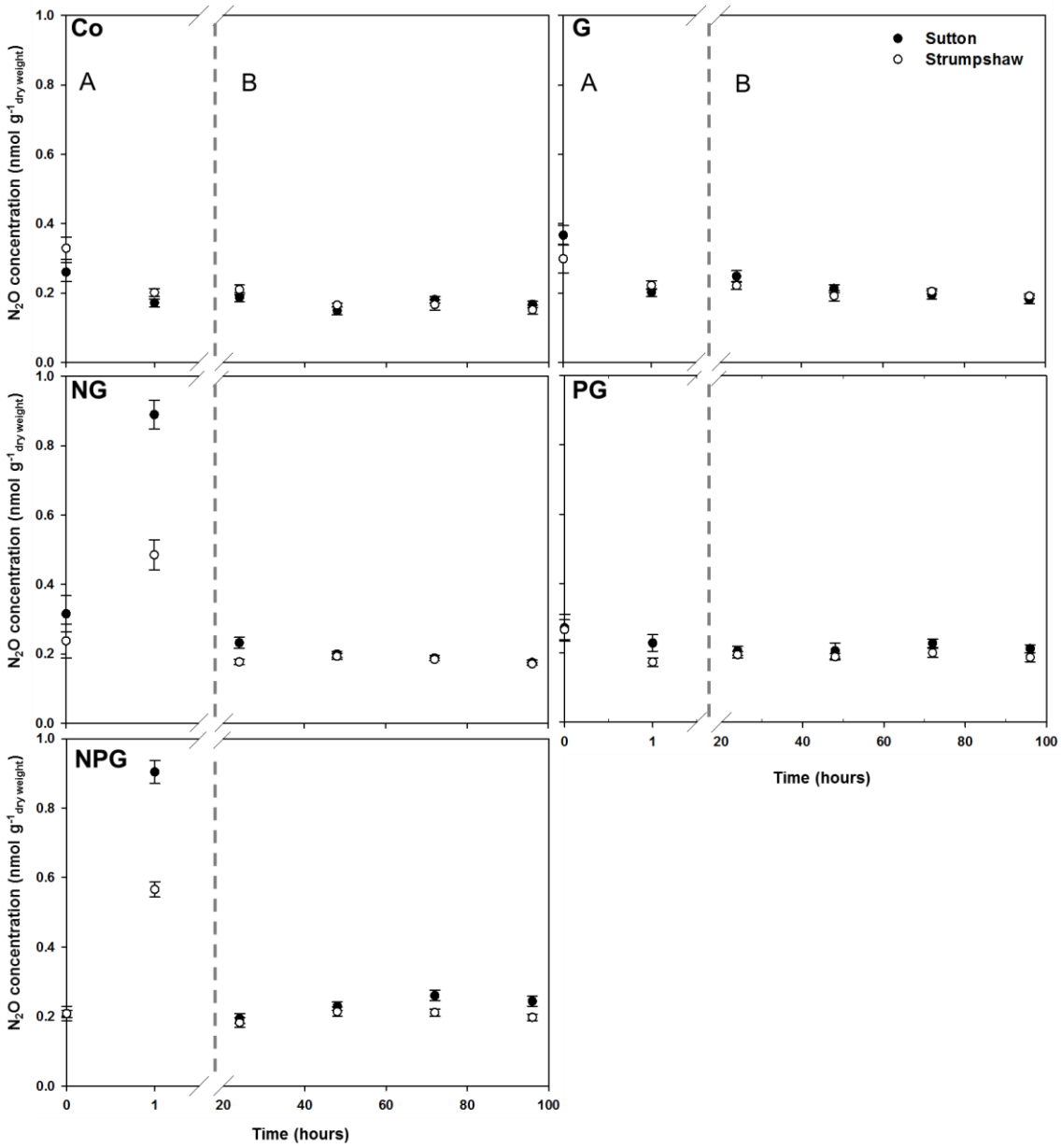


Figure 94 Potential N_2O production for control (Co), glucose (G), nitrate + glucose (NG), phosphate + glucose (PG) and nitrate + phosphate + glucose NPG treatments for nutrient-poor (Sutton Fen) and nutrient-rich (Strumpshaw Fen) peat. Section A represents potential N_2O production time period, whilst section B delineates the period after production. Points represent mean values and error bars denote ± 1 standard error.

7.3.2 Microbial biomass

Microbial biomass obtained by SIR is shown in Figure 95 and Table 63. No clear difference was observed between sites in the pre-experiment SIR results, with only a slight difference in the rate (Table 63) but it was not statistically significant. Both sites showed a steady increase in CO_2 concentration. Post-experiment SIR results show a divergence between the two sites for all of the treatments. Treatments with PO_4^{3-} added showed the greatest increases. Increases post-experiment were significantly greater than pre-experiment and translate into a greater biomass post-experiment (Table 63). SIR and microbial biomass were generally greater at Strumpshaw than at Sutton (Table 63; ANOVA, $F_{1,24} = 36.7$, $p < 0.001$). SIR rates were significantly different between pre- and post-experiment controls (ANCOVA, between factors: pre-/post-experiment, treatment and site, covariate: time; $F_{1,46} = 27.039$, $p < 0.001$) and treatments were significantly different for post-experiment rates (ANCOVA, $F_{4,46} = 2.893$, $p < 0.05$). There was no significant interactions between factors.

Table 63 Substrate induced respiration rates and microbial biomass for each treatment (Pre = pre-experiment control (no N and P additions), Post = Post-experiment control (no N and P additions), G = Glucose, NG = nitrate and glucose, PG = phosphate and glucose and NPG = nitrate, phosphate and glucose) for nutrient-poor (Su = Sutton) and nutrient-rich (St = Strumpshaw) sites.

	Treatment	Site	Mean rate CO_2 (µg $g^{-1}_{dry\ weight}$ h^{-1}) [1 S.E.]	Average total microbial carbon biomass (mg microbial C $g^{-1}_{dry\ weight}$) [1 S.E]
Pre-experiment	Pre	Su	0.9 [0.06]	80 [2]
		St	1.2 [0.28]	142 [15]
Post-experiment	Post	Su	7.6 [0.42]	249 [5]
		St	9.6 [2.7]	411 [80]
	G	Su	9.4 [0.29]	266 [6]
		St	7.3 [0.43]	365 [7]
	NG	Su	6.1 [0.55]	308 [21]
		St	7.5 [0.34]	375 [12]
	PG	Su	8.0 [0.68]	285 [16]
		St	8.9 [0.49]	361 [15]
	NPG	Su	8.9 [0.14]	293 [7]
		St	8.1 [1.0]	423 [13]

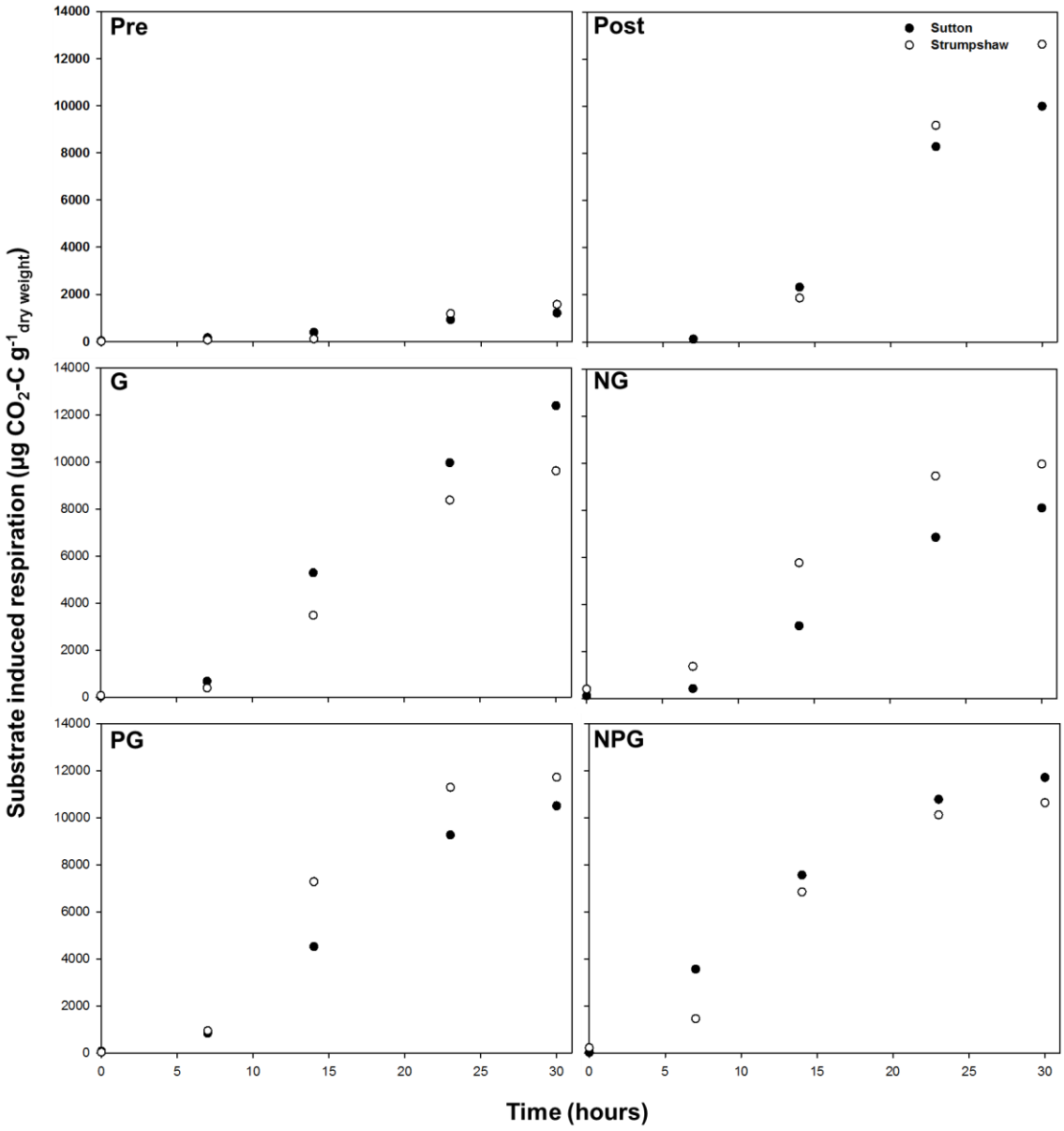


Figure 95 Substrate induced respiration (fertilised – control samples) for pre- (Pre) and post-experiment controls (no N or P fertilisation (Post), glucose (G), NO_3^- + glucose (NG), PO_4^{3-} + glucose (PG) and NO_3^- + PO_4^{3-} + glucose (NPG)) additions. Each point represents a mean of n = 3.

7.3.3 Microbial activity

Microbial activity was measured using the FDA method (Table 64). Little difference in activity was observed pre-experiment between sites. A significant difference between pre- and post-experiment microbial activity was noted for both Sutton (T-test, t_4= 9.253, p < 0.001) and Strumpshaw (T-test, t_4= 16.62, p < 0.001), with activity increasing with the experiment. Microbial activity differed significantly for treatments (post-experiment) for Sutton (ANOVA, $F_{5,12}$= 14.653, p < 0.001) and Strumpshaw (ANOVA, $F_{5,12}$= 11.278,

$p < 0.001$). However, the order of importance for each treatment was different for each site: Sutton Fen: Post>G>NPG>NG>PG and Strumpshaw fen: Post>NPG>G>PG>NG

Table 64 Mean microbial activity [± 1 S.E] measured as rate of FDA hydrolysis (µmol $g^{-1}_{dry\ sediment}$ min^{-1}) for each treatment (Pre = Pre-experiment (no N, P or G additions), Post-experiment (no N, P or G additions), G = Glucose, NG = nitrate and glucose, PG = phosphate and glucose and NPG = nitrate, phosphate and glucose) for nutrient-poor (Su = Sutton) and nutrient-rich (St = Strumpshaw) sites.

	Treatment	Site	Rate of FDA hydrolysis (µg $g^{-1}_{dry\ sediment}$ min^{-1})
Pre-experiment	Pre	Su	147 [± 7]
		St	140 [± 5]
Post-experiment	Post	Su	348 [± 21]
		St	361 [± 12]
	G	Su	255 [± 11]
		St	287 [± 33]
	NG	Su	238 [± 34]
		St	208 [± 35]
	PG	Su	200 [± 4]
		St	238 [± 15]
	NPG	Su	242 [± 8]
		St	292 [± 20]

7.4 Discussion

This study demonstrates that fertilisation of floodplain fen peat with NO_3^-, PO_4^{3-} and labile C (glucose) alters potential GHG production (Table 62). Relatively few studies have quantified anaerobic potential GHG production, such as Updegraff et al. (1995) and Bridgham et al. (1998), and even fewer have measured the changes to GHG production with N and P fertilisation under anaerobic conditions. No study has looked at how NO_3^- and PO_4^{3-} additions alter C and N mineralisation under anaerobic conditions in floodplain fens, making this study novel. Samples used in this study were disturbed before and during the experiment and were incubated over a short period of time; therefore, fluxes represent potential production of CO_2, CH_4 and N_2O and cannot be compared with field fluxes (Glatzel et al., 2004).

The following research question and hypotheses are answered within this chapter:

R.Q.7. How does potential production of CO_2, CH_4 and N_2O change with fertilisation of N and P loads in nutrient-rich and nutrient-poor floodplain fen peat?

H_{11}: Potential CO_2, CH_4 and N_2O production will be greater in nutrient-rich than in nutrient-poor peat.

H_{12}: NPG fertilisation will increase potential CO_2 and N_2O production rates more than other treatments.

H_{13}: PG fertilisation will increase potential CH_4 production rates more than other treatments the most.

7.4.1 Effects of treatment on microbial biomass and activity

Significant alterations in microbial biomass (t_4 = -31.601, p < 0.001 and t_4 = -3.318, p = 0.029 for Sutton and Strumpshaw, respectively) and activity (t_4 = -9.253, p < 0.001 and t_4 = -16.62, p < 0.001) were observed in the no addition treatments pre- and post-experiment (Table 63 and 64). The increase in microbial biomass and activity over the 15 day experiment was expected due to k-strategist mineralisation and an increase in temperature from sample storage to incubation of samples at 16 °C. Temperature is known to alter microbial biomass abundance, composition and activity, and will affect C mineralisation processes (Zogg et al., 1997).

Significant differences were also seen between the post-experiment treatments for both microbial biomass (Table 63) and activity (Table 64). All nutrient additions (N, P and G) increased microbial biomass significantly for Sutton Fen peat (Table 63) in comparison to the post-treatment non-additions samples; however, NPG additions increased the microbial biomass the most. Fertilisation with both N and P increased microbial biomass within the nutrient-poor fen peat. This pattern was not observed in Strumpshaw Fen peat, as only NPG samples had a greater microbial biomass than the post-experiment non-addition samples. Differences in response between sites may be due to differences in microbial C:N:P ratios (section 3.2.2), which control rates of mineralisation and immobilisation. OM decomposition decreases C:N and C:P ratios to that of microbes, with N and P being immobilised and C released for mineralisation until critical C:N and/or C:P ratios are reached (Wang et al., 2014a). Critical C:N and C:P ratios have not been

quantified for peatlands but are ~ 40 and ~ 1000, respectively, in Canadian forest litters (Moore et al., 2011, Wang et al., 2014a). However, critical ratios may be different between sites due to the difference in nutrient status, microbial biomass and activity between the two sites. Additionally, Moore et al. (2011) observed a negative correlation ($R = -0.6$, $p < 0.05$) between peat C:N ratios and CO_2 production within peat. Microbial activity was significantly less in fertilised samples than non-fertilised post-experiment samples (Table 64). The addition of nutrients allowed r-strategist microbes to outcompete k-strategist microbes, resulting in less activity in k-strategists at the end of the experiment. Additionally, N and P amendments have been shown to reduce microbial activity in mineral soils due to alterations in soil pH (Söderström et al., 1983, Andersson and Nilsson, 2001); however, pH was not measured in this study.

Glucose additions led to significantly greater microbial biomass ($t_4 = -29.411$, $p < 0.001$ and $t_4 = -13.522$, $p < 0.001$ for Sutton and Strumpshaw, respectively) and activity ($t_4 = -8.214$, $p < 0.001$ and $t_4 = -4.361$, $p = 0.012$) following the experiment compared to before incubation. However, there was no significant difference between post-experiment control and glucose addition samples to microbial biomass and activity. The lack of difference between post-experiment controls' and glucose amendments' microbial biomass and activity is a function of the methods used to ascertain biomass and activity. The two methods measure active biomass and activity and hence by the end of the experiment, the r-strategist microbes have used the entire available labile C from the glucose (shown in Figure 64), resulting in a lack of substrate and therefore reduce their activity and biomass. This is not noticed in the control samples as there is no additional labile C source, hence the k-strategist microbes are mineralising C. As the k-strategist microbes are not limited by C source as they mineralise more recalcitrant forms of C, they function until the end of the experiment. Therefore, comparisons between microbial biomass and activity are more logical between pre- and post-experiment values, rather than between post-experiment treatments.

7.4.2 Effects of treatment on potential GHG production

Potential CO_2, CH_4 and N_2O production was found to be within reported anaerobic literature values (Table 65). Potential CO_2 production within control samples decreased initially from the start of the experiment to 96 hours, whilst CH_4 concentrations increased steadily at both sites. This would suggest the reduction of CO_2 either by hydrogenotrophic methanogens or by acetogenic bacteria and then the subsequent acetoclastic methanogenesis. The former process has been observed in a number of

peatlands, including both ombrotrophic and minerotrophic peatlands (Duddleston et al., 2002, Horn et al., 2003, Keller and Bridgham, 2007), reducing CO_2 and H_2 to form CH_4. Acetogenic bacteria reduce CO_2 to acetate (Drake et al., 2002), which can then be used by acetoclastic methanotrophs to form CH_4. Acetoclastic methanogenesis is generally the more dominant process within fens due to the acetoclastic methanogens being neutrophillic (Horn et al., 2003, Keller and Bridgham, 2007). The alteration in CO_2 response from 96 hours in control samples may be due to anaerobic CO_2 production via fermentation becoming greater than CO_2 reduction (Figure 92Co). This also affects potential CH_4 production (192 hours; Fig 93Co), as simple compounds formed during the fermentation process are available for acetoclastic and hydrogenotrophic methanogens (Keller and Bridgham, 2007). The drop in N_2O over the experiment suggests the reduction of the gas, possibly for CO_2 production. However, N_2 concentrations were not measured in this experiment and cannot back up this hypothesis. The results are in line with Deyan and Changchun (2010), who also saw a decrease in N_2O with time but did not suggest a mechanism for the reduction.

In all fertilised samples (G, NG, PG and NPG), a divergence in CH_4 patterns was observed after 144 hours (Figure 93). Samples from Strumpshaw saw a continuation in CH_4 production; however, samples from Sutton Fen all reduced (Figure 93), indicating CH_4 oxidation. Due to the anaerobic conditions within the serum bottles, normal aerobic methanotrophy cannot take place. Two potential routes for anaerobic CH_4 oxidation (AOM) are postulated within the literature: i) AOM coupled with denitrification using NO_3^- or NO_2^- (section 2.3.4.3) or ii) AOM via anammox (section 2.3.4.2) (Smemo and Yavitt, 2007, Ettwig et al., 2010, Smemo and Yavitt, 2011, Blazewicz et al., 2012). AOM coupled with denitrification has been shown to occur within peatlands with regular N inputs and a large denitrifying population (Blazewicz et al., 2012, Gupta et al., 2013). There is a large possibility that the AOM in Sutton Fen fertilised samples is due to AOM coupled with denitrification due to the availability of inorganic forms of N from ammonification, which is closely coupled with C mineralisation processes. The anaerobic conditions would promote more N_2 production rather than N_2O production and it was not possible to measure N_2 in this study. The second process, AOM coupled with anammox, has not been observed in peatlands but in other wetlands environments (Zhu et al., 2010, Smemo and Yavitt, 2011). Oxygenase enzymes tend to be non-specific and can use CH_4 and NH_4^+ interchangeably (Smemo and Yavitt, 2011). However, this process is less likely as anammox bacteria are not known to be ubiquitous in wetland environments (Zhu et al., 2010, Smemo and Yavitt, 2011).

Table 65 Literature comparison for potential CO_2, CH_4 and N_2O production. Mean ± 1 S.E. (range in potential production) shown for CO_2, CH_4 and N_2O.

Reference	CO_2 (nmol g^{-1} h^{-1})	CH_4 (nmol g^{-1} h^{-1})	N_2O (nmol g^{-1} h^{-1})	Site type	Comments
van den Pol-van Dasselaar and Oenema (1999)		(0 – 0.52)		Floodplain fen	Incubation at 20 °C
Deyan and Changchun (2010)			(0 – 7.02) (0 – 3.2)	Floodplain fen	NO_3^- additions PO_4^{3-} additions
Well et al. (2003)			5.1 ± 4.6 3.5 ± 1.6	Fen	Müncheberg fen Paulineneue fen
Scanlon and Moore (2000)	(2 – 90)			Fen	
Updegraff et al. (1995)	500 700	223 528		Fen	Incubation at 15 °C Incubation at 30 °C
Glenn et al. (1993)	(700 – 1300)			Drained fen	CH_4 consumption 0 – 0.54 nmol g^{-1} h^{-1}.
Francez et al. (2000)	(90 – 630)	(0 – 14)		Raised-bog	
Glatzel et al. (2004)	(10 – 300)	(0 – 2120)		Bog	Incubation at 20 °C, highest potential production from revegetated bog's surface
Yavitt et al. (1997)	(420 – 2500)	(0 – 19)		Bog	Incubation at 12 °C
Moore and Dalva (1997)	(70– 1600)	(0.03 – 260)		Peatland	Incubation at 20 °C

7.4.2.1 Glucose additions

Glucose additions significantly increased CH_4 potential production at both sites (Figure 93; Table 62). This corroborates research by Yavitt et al. (1997) in Minnesota peatlands, where potential CH_4 production was between two to eight times greater with G additions. The stimulation of methanogens in fertilised samples is likely to be caused by the addition of a labile C source for r-strategist microbes to mineralise. Alterations to CH_4 production were greater in peat from Sutton and Strumpshaw fens than in Yavitt et al. (1997), with an increase in CH_4 fluxes by two orders of magnitude. After 144 hours, the pattern changed in Sutton Fen slurries from CH_4 production (3.7 ± 0.43 nmol $g^{-1}_{dry\ weight}$ h^{-1}) to greater CH_4 oxidation (-0.53 ± 0.1 nmol $g^{-}_{dry\ weight}$ h^{-1}, negative equates to CH_4 oxidation). This pattern has not been observed in other aerobic or anaerobic peat microcosm studies. CO_2 production did not alter as significantly from control samples (Figure 92Co); however, there was a small increase in production, especially after 96 hours (ANCOVA, $F_{1,11}$ = 8.588, p = 0.014 and $F_{1,11}$ = 15.909, p = 0.002 for Sutton and Strumpshaw, respectively). The minor alteration to potential CO_2 production also agrees with Yavitt et al. (1997) findings. N_2O concentrations decreased as in the control samples (Figure 94) due to a lack of bioavailable N for denitrification to occur.

7.4.2.2 NO_3^- additions

N_2O was only produced in the two treatments where NO_3^- was added (NG and NPG; Figure 94), as observed in Deyan and Changchun (2010). There was no significant difference between potential N_2O production in either NG or NPG amendments for either Sutton and Strumpshaw peat and was not anticipated (H_{12}). It was thought that the NPG amendments would significantly increase N_2O production as there would be more reactants from the P additions for denitrifiers. Non-NO_3^- amendments (C, G and PG) did not lead to N_2O production. These results are contrary to Deyan and Changchun (2010), where N_2O production increased with P amendments of up to 1 mg P $g^{-1}_{dry\ weight}$. Differences in bioavailable N are thought to be the reason for the difference between the two studies. Deyan and Changchun (2010) cite concentrations of 317 mg kg^{-1} available N within the substrate used for the study. Bioavailable N was not measured for Sutton and Strumpshaw fen but as N_2O was produced in the N-amended sample, and conditions were identical for each treatment. Therefore, denitrifying bacteria are present within the substrate but there is a lack of bioavailable N in the peat.

CO_2 fluxes were not significantly different between the two N treatments, nor in comparison with control samples (H_{12}). This was not expected; it was thought that

fertilisation with NPG would significantly increase fermentation due to increased reactants and an energy source (H_{12}). Therefore, H_{12} was rejected. CO_2 production was also altered at the beginning of the experiment in the NG amended samples, with the highest production 1 hour after fertilisation. The increase was more marked for Sutton samples (Figure 92NGa), as in the N_2O production (Figure 94NG), than for Strumpshaw samples. The greater initial biomass in Strumpshaw samples (Table 63) may be the causal factor for differences observed. Due to the larger biomass and higher N contents in biomass, NO_3^- is immobilised rather than increasing the activity and producing N_2O. Additionally, microbial populations that are N limited are able to increase their biomass and activity when there is an increase in bioavailable N (Treseder, 2008). It has been shown in a number of environments, N additions have been found to reduce microbial biomass and activity in microbial populations that are not N limited. Reductions in biomass and activity are caused by altering substrate pH and ligninase activity (Söderström et al., 1983, Treseder, 2008). The latter process changes microbes' ability to access other compounds for C and energy by reducing ligninase production and prevents the breakdown of lignin that often binds many other compounds together (Treseder, 2008). The reduction in CO_2 production from N addition was not observed in this study. Instead an increase in CO_2 production was seen within the first hour after fertilisation, indicating that O_2 possibly became available during the denitrification process for respiration.

The inhibiting effect of N additions is also seen in CH_4 potential production. Despite the glucose addition in both N amendments increasing potential CH_4 production, fluxes were significantly less than glucose only additions for NPG additions ($U_{12} = 0.001$, $Z = -1.086$, $p = 0.03$ and $U_{12} = 0.001$, $Z = -3.13$, $p = 0.02$ for Sutton and Strumpshaw, respectively) and NG additions (Strumpshaw only: $U_{12} = 0.001$, $Z = -3.136$, $p = 0.002$). NO_3^- is known to be a non-specific methanogen inhibitor (section 2.3.3.2) as well as being shown to act as an electron acceptor in anaerobic CH_4 oxidation (section 2.3.3.3) (Smemo and Yavitt, 2011). Despite the availability of NO_3^- at the beginning of the experiment, AOM was not observed after starting the experiment as CH_4 concentrations were similar between all treatments. Additionally, most NO_3^- from the fertilisation solutions would be used by denitrifying bacteria first as CH_4 concentrations were not significant enough for AOM to occur. The use of NO_3^- at the beginning of the experiment by denitrifiers would explain the smaller oxidative rates after 144 hours for Sutton Fen peat slurries with N additions (-0.19 ± 0.01 and -0.2 ± 0.08 nmol $g^{-1}_{\text{dry weight}}$ h^{-1} for NG and NPG, respectively), as NO_3^- would have been immobilised into organic forms of N.

7.4.2.3 PO_4^{3-} additions

PG fertilisation significantly increased potential anaerobic CO_2 production more than other treatments from 96 hours to the end of the experiment in Strumpshaw Fen's samples (ANCOVA, $F_{4,29} = 3.469$, $p = 0.02$). This response was not anticipated, as it was thought that NPG fertilisation would increase potential CO_2 production the most (H_{12}) as there would be a greater source of reactants for fermentation. There was no significant difference between treatments for Sutton Fen's samples. At present, there are no other anaerobic potential experiments that fertilised samples with PO_4^{3-}. However, Amador and Jones (1993) found that fertilisation of aerobic peat slurries with PO_4^{3-} significantly increased potential aerobic CO_2 production in peat samples with a similar C:P ratio to Strumpshaw fen. Additionally, Amador and Jones (1993) found that in peat with a low total P content, similar to Sutton fen, PO_4^{3-} amendments of 1.1 mg L^{-1} inhibited CO_2 production by altering the C:P ratio to a point where C assimilation by soil microflora becomes C limited. It is possible that the addition of P did not induce fermentation to the same degree as in Strumpshaw samples due to greater C assimilation. However, this pattern was not noted in the CH_4 response, suggesting that the samples did not become C limited. Instead, it is suggested that the majority of the PO_4^{3-} added was used by methanogens as the conditions were more favourable for methanogenesis by r-strategist microbes with the addition of glucose. As for potential CO_2 production, potential CH_4 production was also the greatest in the PG fertilised samples, resulting in H_{13} being accepted. P fertilised Sutton Fen slurries also had the greatest reduction in CH_4 concentration after 144 hours. These results suggest that microbial C mineralisation in the two substrates is P-limited.

7.4.3 Differences between nutrient-rich and nutrient-poor peat

Highest GHG production was observed in samples fertilised with glucose and nutrients, indicating that peat from the two sites were nutrient and energy limited. Peat from Strumpshaw fen was only P limited, as seen in the potential production of N_2O with N_2O fluxes significantly less at Strumpshaw despite a significantly greater microbial biomass and a significantly lower peat C:N ratio ($U_{30} = 775$, $Z = -1.905$, $p = 0.05$). The greater microbial biomass both before and after the experiment was expected due to the higher nutrient status of the site (section 3.2). Additionally, the greater activity (post-treatment) at Strumpshaw was expected due to the greater biomass and nutrient status of the site.

The difference in peat nutrient status also translated into GHG production. CH_4 production was significantly greater in peat from Strumpshaw fen (Table 62) than Sutton

fen, as hypothesised (H_{11}). The greater microbial biomass in the peat enabled greater mineralisation of C. N_2O followed the converse relationship to CH_4 production with Sutton fen having greater potential N_2O production (Figure 94) in the samples fertilised with NO_3^- (t_{11} = 3.357, p = 0.006 and t_{12} = 8.838, p < 0.001 for NG and NPG samples, respectively). This difference was not anticipated (H_{11}), but thought to be caused by greater N microbial biomass in Strumpshaw's peat due to the greater N inputs to the site (Section 3.2). Unlike CH_4, CO_2 production was not significantly different between sites. The lack of difference may be caused by greater CO_2 reduction by hydrogenotrophic methanogens in Strumpshaw's samples and would help to explain the greater potential CH_4 production. This resulted in H_{11} being partially accepted.

The change in response after 144 hours in CH_4 production at Sutton fen was not anticipated. A linear increase in production was anticipated to the end of the experiment, as observed in fertilised samples from Strumpshaw fen (Figure 92). This difference may be due to the greater microbial biomass and nutrient contents in Strumpshaw's peat. The greater biomass enables Strumpshaw's samples to mineralise the glucose at a faster rate, whilst the higher nutrient contents of the peat allow for greater remineralisation of immobilised nutrients. Based on stoichiometric calculations, glucose additions were used up within the initial 96 hours of the experiment. As the labile C source was used up, it is hypothesised that greater rates of CO_2 reduction occurred, further increasing CH_4 production. There was also an unanticipated divergence in potential CH_4 production after 144 hours, with greater rates of AOM than methanogenesis. This divergence in pattern has not been observed in other aerobic or anaerobic studies.

7.4.4 Flooding of floodplain fens with nutrient-enriched river water

The results from this study cannot simply be scaled up for a site and compared with *in situ* fluxes due to the experimental design, disturbance of samples and removal of roots, rhizomes and vegetation. However, only taking the peat substrate, and not the interactions with vegetation, in a floodplain fen into account during an inundation event with nutrient rich flood water, some of the patterns observed in this study may ensue following the inundation. The chemical composition of the floodwater would, however, play a large role in the microbial response to inundation. Labile C would most probably be added to the site in the form of DOC and POC. DOC concentrations within the River Ant and Yare during the March 2013 flood event ranged from 15 to 20 mg L^{-1}. This potential increase in labile C would possibly increase C mineralisation either via heterotrophic respiration if anaerobic conditions had not year been reached or via

fermentation and methanogenesis if under anaerobic conditions. An initial pulse of N_2O would be expected with N inputs via the floodwater. This would be followed by a period of anaerobic CO_2 and CH_4 production. Depending on the floodwater matrix, significant increases in production could occur, although with N additions CH_4 production may not as great as P additions, as seen in Figure 93.

Additionally, the residence time of the floodwater would play an important role in the extent of alterations to GHG cycles. If large flood events occur, like those observed in January and March 2012, where floodwater remained on the sites for a sustained period of time (> 7 days; Figure 32), divergence in patterns may occur between sites. The change in pattern for potential CH_4 production may occur if there is a lack of labile C for the nutrient-poor site after 6 days, with the reduction in methanogenesis and a possible increase in AOM. The microbial biomass, activity and nutrient status of the site would also play a large role in the dynamics of GHG production under a flood event with nutrient-enriched floodwater. A site with a greater nutrient status, such as Strumpshaw Fen (section 3.2), would have a greater microbial biomass and possibly activity, resulting in greater CH_4 production but less N_2O production as observed in this study (Figure 94). Little difference in potential CO_2 production was found between the two sites, Sutton and Strumpshaw Fen, in the incubation experiment; however under whole ecosystem conditions, a difference may occur (as observed in the 16 month sampling period, section 4) with other environmental factors controlling respiration and fermentation.

7.5 Summary and synthesis

The peat microcosm fertilisation study showed the addition of N and P to the peat substrate alters GHG cycles under anaerobic conditions. Fertilisation with NO_3^- was found to significantly increase N_2O production via denitrification but had the opposite effect on methanogenesis, which was inhibited by the addition of NO_3^-, as observed in aerobic studies. The extent of the NO_3^- alterations also depended on the nutrient content and microbial biomass of the peat prior to the experiment. Peat from Sutton had significantly greater N_2O fluxes than Strumpshaw but significantly smaller CH_4 fluxes due to differences in peat C:N ratio and a greater biomass in Strumpshaw Fen peat. PO_4^{3-} additions stimulated methanogenesis the most out of all treatments, as in aerobic studies, suggesting that microbes in both sites were P limited. Anaerobic fermentation was not significantly altered with N and P additions. The lack of difference between fertilised and unfertilised samples on heterotrophic respiration was not observed in other

aerobic studies, which have reported increases in potential production with PO_4^{3-} fertilisation but decreases with NO_3^- additions.

Taking the findings from this microcosm fertilisation experiment into account, it is anticipated that inundation of floodplain fen peat would have a similar response; stimulation of methanogens and denitrifying bacteria causing an initial pulse in N_2O production if a bioavailable N source was present in the floodwater, followed by an increase in CH_4 production. CO_2 production via fermentation would not be expected to alter significantly with a nutrient pulse via inundation. The greatest alterations to GHG production would be seen in CH_4 and N_2O production, as the two gases have a global warming potential 25 and 298, respectively, times greater than CO_2.

8. Conclusions and future research

This research into greenhouse gas (GHG) exchange from floodplain fens of differing nutrient status has quantified carbon (C) exchange within floodplain fens under conservation management and investigated alterations to the C and nitrogen (N) cycles with nutrient loading from fluvial sources. Previously, relatively few studies had been conducted on lowland fens due to the lesser aerial extent in the UK, leaving a knowledge gap in peatland GHG exchange and resulting in biased GHG inventories. The study also elucidated alterations to potential GHG production from floodplain fen peat with N and phosphorous (P) fertilisation in a laboratory microcosm study. With climate change intensifying the hydrological cycle and periods of extreme events, climate models have shown an increasing probability and magnitude in flood events. Current EU and UK policy to help alleviate flooding on urban environments is based on flooding riparian environments, such as floodplain fens. However, the impacts of these flood events on GHG exchange in floodplain fens are not currently well understood and there is a clear need to improve our knowledge.

The main empirical findings from this research are chapter-specific and are summarised within the respective chapters: Site description and nutrient status (chapter 3), Greenhouse gas exchange and controlling factors on carbon fluxes in floodplain fen sites of contrasting nutrient status (chapter 4), Methane emissions via ebullition in floodplain fens of differing nutrient status (chapter 5), Annual carbon exchange from floodplain fen sites of contrasting nutrient status (chapter 6) and Potential greenhouse gas production (chapter 7). This chapter synthesises empirical findings in order to answer the main aim of this research: What is the impact of nutrient loading on GHG exchange in floodplain fens. Section 8.1 presents findings from the research and outlines limitations with the study. Section 8.2 suggests future research ideas stemming from results from this study.

8.1 Research overview

This research has produced four main outcomes that will help to advance knowledge in peatland biogeochemistry.

Firstly, the field campaign quantified *in situ* GHG exchange over a 16 month period between two floodplain fens of differing nutrient status under conservation management. The two sites chosen for this study, Sutton and Strumpshaw Fen, differed in nutrient

status, with surface peat taken prior to March 2013 and foliar N and P contents, as well as plant height and biomass, being significantly greater at Strumpshaw Fen (section 3.3), as hypothesised ($H_{1,2\ \&\ 3}$) due to the larger agricultural catchment and historical sewage inputs. This resulted in plants being largely N limited at Strumpshaw Fen; whilst half of the collars at Sutton Fen were N limited and the remaining collars were P limited based on foliar N:P:K ratios (section 3.3.5). It was anticipated that this greater nutrient status at Strumpshaw Fen would have greater CO_2 and CH_4 fluxes. Annual R_{eco} and GPP were significantly greater at Strumpshaw Fen, the nutrient enriched site. However, annual CH_4 emissions (18 ± 2.6 and 15 ± 1.7 g CH_4 m^{-2} yr^{-1} for Sutton and Strumpshaw Fen, respectively) were similar between sites and therefore H_8 was partially rejected. A significant difference in ebullitive fluxes was observed between sites, with Sutton Fen emitting more CH_4 than Strumpshaw Fen (section 5.3.1), resulting in H_7 being rejected (as it was thought that the nutrient enriched site would have higher ebullitive fluxes). Interestingly, SRP and NO_3^- were shown to be controlling factors on CH_4 emission via diffusive and plant-mediated fluxes (section 4.3.6) and ebullition (section 5.3.2), despite no significant difference in annual CH_4 emission between sites being observed. Significant differences in annual R_{eco} and GPP between sites translated into a difference in NEE between sites, with Strumpshaw Fen acting as a net sink between 1st September 2012 and 31st August 2013, whilst Sutton Fen was a net source of C over the same one year period (section 6.4). The difference between the two sites is due to differences in vascular green area (VGA), which was shown to be one of the main controlling factors on GPP (section 4.3.6). The greater aboveground biomass at Strumpshaw Fen due to the higher nutrient status at the site (section 3.3) resulted in greater GPP. However, the greater VGA and nutrient status also had an impact on R_{eco} (section 4.3.6), resulting in a greater efflux of CO_2 at Strumpshaw Fen than Sutton fen. The smaller VGA and lesser porewater nutrient concentrations at Sutton Fen resulted in smaller GPP and R_{eco}. SRP and NO_3^- were also found to be controlling factors on R_{eco} (section 4.3.6). Only SRP was shown to have a controlling factor on GPP (section 4.3), despite only 3 collars at Sutton and one collar at Strumpshaw being P limited (section 3.3.5). These results indicate that nutrient enrichment of a site via fluvial sources does not necessarily have a negative impact on C dynamics within floodplain fens over a mid- to long-period (> 1 month) and may potentially enable greater CO_2 sequestration within a site, if the right conditions prevail.

Secondly, the effects of nutrient enriched flood events were also observed during the 16 month sampling period. Two significant flood events occurred in early January and March 2013 (Figure 32), with different responses observed after each of the flood events. The

January 2013 flood event caused an increase in surface peat temperature from 1 °C to 5 °C, increasing CH_4 emission, R_{eco} and NEE (emission of CO_2) than in the pre- and succeeding sampling months (November 2012 and March 2013) due to the creation of a thermal buffer and the influx of NO_3^- and SRP into the sites, introducing nutrients that can be used as reactants for methanogenesis, respiration and fermentation. The introduction of NO_3^- and PO_4^{3-} in the *ex situ* microcosm study (chapter 7) showed an initial pulse of potential N_2O production after NO_3^- additions (Figure 94; section 7.3.1) and a significant increase in potential CH_4 production with PO_4^{3-} additions (Figure 93; section 7.3.1). Despite the microcosm study being undertaken on disturbed peat samples and under specific conditions, it illustrates alterations to anaerobic processes, such as denitrification and methanogenesis, which may occur with inundation of floodplain fens with nutrient enriched flood water. The flood event in March 2013 inundated the two sites to a greater extent than the January 2013 event, increasing the water level to > 20 cm above the peat surface (Figure 32). This flood event brought in large amounts of NO_3^- in a soluble form (Figure 26 and 28) and potentially in a sediment-bound form; although sediment deposition was observed, it was not quantified, nor the concentrations of N and P bound to the sediment. A drop in CH_4 emission, R_{eco} and NEE (from emission to a net uptake) was observed in March 2013 (Figure 41 and 51; section 4.3) and is thought to be due to the large amounts of water and sediment brought into the site, inducing anaerobic conditions and therefore reducing respiration. The potential causal factors on the reduction in CH_4 emission include the inundation of the sites with NO_3^- rich waters, which has been shown to be a methanogen inhibitor both in the literature and within this study in the microcosm fertilisation experiment (section 7.3.1; Figure 93); the increase in turbid water reducing photosynthesis and therefore root exudate release; and the augmentation of a water body on top of the peat surface altering transport pathways from diffusive to evasive, resulting in the water body needing to be super saturated prior to CH_4 efflux.

Timing plays a large role in how GHG exchange alters in response to flood events. The second flood event had a greater effect on the sites due to the timing of the event, which occurred at the beginning of the growing season and left water above the peat surface for a couple of months (Figure 32; section 3.3.7). This had a dramatic impact on plant growth dynamics, putting stress on plant species with an early growing season like sedges and significantly reduced the VGA at Sutton Fen, where there is a greater abundance of plant species with an early growing season (section 3.3.3 and 4.3.2). The high water levels did not impact Strumpshaw Fen as significantly due to the greater abundance of graminoids, especially *P. australis*, which have a later growing season

than sedges and are more used to such prevailing conditions (Grime et al., 2007). Strumpshaw Fen had a greater VGA during the 2013 summer months thanks to the increased nutrient inputs from the flood event and, potentially, the lack of competition at the beginning of their growing season reducing shading stress. A significant difference was noted in surface (top 15 cm) peat N and P contents before March 2013 and in June 2013 (section 3.2.2). This increase in N and P may account for the greater VGA at Strumpshaw Fen in 2013, possibly causing the greater annual R_{eco}, captured within the mixed-effects model by the greater VGA. The alterations to the VGA at both sites also caused changes in GPP between the two sites, which was significantly less in 2013 at Sutton Fen than in 2012 (Figure 42). This reduction in GPP wasn't observed at Strumpshaw Fen, especially with the greater VGA in August and September 2013 than the previous year.

Flooding duration also has a large impact on GHG exchange, altering plants ability to survive. Events occurring near the beginning of growing season have a greater detrimental impact on plants, as plants are more prone to stress at this stage in the growing season. The amount of reserve carbohydrates in plant's rhizomes dictates the maximum water level that shoots can overgrow at the beginning of next growing season (Blom, 1999, Koebsch et al., 2013a). Reserve carbohydrates are dependent on the previous year's growth, with greater amounts stored with greater plant growth (Blom, 1999, Koebsch et al., 2013a). There are certain plants that can survive long periods of flooding, such as *Carex spp., which* can survive up to 40 days fully submerged (Moog, 1998). Other species have developed other means to cope with long durations of flooding stress, such as *P. australis* producing fewer but taller culms (Vretare et al., 2001, Koebsch et al., 2013a).

Alterations to GHG exchange also depend on the chemistry of the floodwater as well as timing, magnitude and duration of the flood event. The floodwater chemistry was not thoroughly investigated in this study in the two winter 2013 events. There is, however, water chemistry data for the day after the March 2013 event occurred (Figure 25 to 30; section 3.3.6), with increases in river water NO_3^-, SO_4^{2-} and Cl^- concentrations. Similar increases in macronutrient concentrations were not observed in ditch or porewater, indicating the possible uptake of nutrients by plants and microbes. Environmental impacts are always difficult to elucidate in *in situ* studies due to the inherent complexity of natural environments, therefore a single macronutrient cannot be singled out for a reduction in fluxes. However, SO_4^{2-} has previously been shown in other studies to reduce

methanogenesis due to the competition for labile C by sulphate reducing bacteria (Dise and Verry, 2001, Gauci et al., 2004, Gauci et al., 2005); salinity alters solubility of CH_4 and CO_2 (Weiss, 1974, Yamamoto et al., 1976), reducing the aqueous concentrations of gases and potentially making water bodies less supersaturated. For example, aquatic CO_2 and CH_4 would decrease by 11 and 1.1 %, respectively, with an increase in salinity from 0 ppt to 36 ppt at 0 °C. However, SO_4^{2-} was not shown to be a controlling factor on CH_4 emission, R_{eco} or GPP (Table 33; section 4.3.6). NO_3^- has been shown in this study (section 7.3), and in other studies (Smemo and Yavitt, 2011), to suppress potential CH_4 production as NO_3^- is toxic to methanogenic archaea (Roy and Conrad, 1999, Smemo and Yavitt, 2011). Roy and Conrad (1999) did not state a NO_3^- concentration threshold for toxicity to methanogenic archaea; however, Watson and Nedwell (1998) simulated NO_3^- deposition on ombrotrophic peat in a laboratory-based study and found that 1.4 mg L^{-1} NO_3^--N significantly decreased CH_4 formation, whilst smaller concentrations of NO_3^- had no significant effect. This observed threshold may be different in floodplain fens; however, no other fen study has quantified NO_3^- impacts on methanogenesis using a range in NO_3^- concentrations. Additions to peat substrate for the microcosm fertilisation experiment (section 7.3) were 51 mg L^{-1} (based on a threefold increase in maximum observed riverine NO_3^- concentrations), significantly greater than in Watson and Nedwell (1998), with methanogenesis suppression observed at this NO_3^- concentration. However, only one concentration of NO_3^- was used in this study, preventing the elucidation of a threshold concentration for alterations to potential methanogenesis. River Ant and Yare NO_3^-N concentrations were frequently observed to be greater than the threshold observed in Watson and Nedwell (1998), especially during January and March 2013 when the two main flood events occurred.

Thirdly, ebullition is an extremely important transport mechanism for CH_4 release to the atmosphere in floodplain fens, with observed fluxes within a similar order of magnitude to diffusive and plant-mediated fluxes (section 4.3.4 and 5.3). No previous study has quantified ebullition in floodplain fens and has shown fluxes to be within a similar order of magnitude to diffusive/plant-mediated fluxes. Ebullition rates were shown to be significantly greater at Sutton Fen, the nutrient poorer site, than at Strumpshaw Fen, resulting in H_7 being rejected. Additionally, no previous study has looked at ebullition over two different time periods, as done within this study from March 2013 onwards. For environments with high C exchange, such as floodplain fens, shorter runs (< 48 hours) to quantify rates of ebullition give a more representative flux as oxidative process are not as great on free-phase CH_4 gas bubble build-up within the gas funnel traps (section 5.4.2.2). It is suggested that shorter runs (< 48 hours) should be used to quantify

ebullition in highly productive sites, such as floodplain fens. Relatively few studies into ebullition have tried to elucidate controlling factors on episodic ebullition. This study showed the importance of pressure alterations on ebullition, with a fall in minimum barometric pressure shown to be the most important controlling factor on ebullition at Sutton and Strumpshaw Fen, followed by water level, peat temperature, barometric pressure and a suite of porewater macronutrients. This study is the first to show that porewater nutrients affect ebullition rates.

Finally, the findings from the *ex situ* laboratory microcosm fertilisation experiments allowed for the elucidation of alterations to potential CO_2, CH_4 and N_2O production under anaerobic conditions. With inundation of floodplain fens, anaerobic conditions will ensue and alterations to fermentation, methanogenesis and denitrification may occur with nutrient additions. Results showed that inundation with N and P has the potential to increase potential GHG production (Section 7.3.1). Fertilisation with SRP increases potential CH_4 production the most (H_{13}), whilst NO_3^- additions inhibited CH_4 production due to its toxicity to methanogens (section 7.4.2). Only additions of NO_3^- increased N_2O production through the addition of a substrate for denitrification. Both CH_4 and N_2O have a higher GWP (25 and 294, respectively over a 100-year horizon) than CO_2 and need to have emissions reduced to help reduce GHG emissions. No significant alterations occurred with potential CO_2 production under anaerobic conditions (H_{12} rejected), corroborated by Aerts and Toet (1997), and very small amounts of CO_2 were produced during the experiment. These results are different to studies done under oxic conditions, where N and P additions increased respiration from marsh sediments (with low concentrations for P; < 32 mg L^{-1} P) (Amador and Jones, 1993).

Taking the results from this study into account on alterations to GHG exchange from fluvial nutrient loading, flood policy can be informed to significantly reduce emissions during and post flood events. Nutrient enrichment does not strictly have a negative impact on C exchange within floodplain fens in the mid- to long-term (> 1 month), as it can help to increase CO_2 sequestration with increases to aboveground green biomass. However, nutrient enrichment can induce pulses in N_2O and CH_4 emissions. These two gases are more potent GHGs on a molecule-per-molecule basis in comparison with CO_2 and therefore it is necessary to try to reduce emissions. Nutrient enrichment also has a significant effect on biodiversity within floodplain fens, which has not been covered within this research.

Controls and incentives are a means to try to reduce nutrient inputs into the catchments, with the latter often resulting in better outcomes (Morris et al., 2000). Economic incentives given to significant aquatic polluters, such as farmers, to reduce their nutrient input into rivers has been shown to help reduce aquatic nutrient loads (Morris et al., 2000). Therefore, the reduction in both organic and inorganic fertiliser usage should be encouraged using both national and European policy (Natural England, 2009, European Commission, 2013, Warner et al., 2013), such as agri-environmental schemes and the common agricultural policy, and more dynamic means of cropping rotations and set aside land to help naturally increase nutrient inputs into soil and reduce nutrient leaching and inputs into the aquatic ecosystem. Benefits from a reduction in fertiliser usage would not only propagate out to rivers and floodplain fens, but to other floodplain fen environments, such as mineral soils. Controls on mineralisation processes within mineral soils are different to those in peat; however, nutrient inputs have been shown to increase heterotrophic respiration, methanogenesis and denitrification in mineral soils (Van Cleve and Moore, 1978, Mosier et al., 1991, Smith et al., 1998, Peng et al., 2011).

In floodplain fen sites located in agricultural environments, like Sutton and Strumpshaw Fen, flood water should be allowed off site as soon as possible to reduce GHG emissions and stress on vegetation, especially if at the beginning of the growing season. In turn flood events will have a reduced impact on plant dynamics and a lesser impact on GPP, unlike the patterns observed at Sutton Fen in 2013. Inundation later in growing season does not have such a dramatic impact on vegetation as plants aerenchyma's have developed and can oxidise the rhizosphere. The results from this study can also impact on management of floodplain fen sites as it can inform site managers of the potential impacts of inundating sites when nutrient levels in the rivers that feed the floodplain fens are high. To keep emissions low, it is best to inundate sites when the vegetation is least vulnerable, such as in the winter at minimum temperatures or in summer at peak biomass. Results from section 4.3.5 show ditches within floodplain fens to be significant sources of CH_4 and maybe used to alter conservation management practices for the proportion of fen area turned into shallow water bodies to create a mosaic of terrestrial and aquatic environments.

A long-term study into floodplain fen GHG exchange is, however, needed to fully understand the interactions of flooding a site during differing time of the year with nutrient rich water.

8.2 Future research

A number of further research ideas have arisen from this work, outlined in the following subsections.

8.2.1 Long term monitoring of GHG exchange in floodplain fens.

A long-term study in GHG exchange in floodplain fens of differing nutrient status under conservation management is needed to better understand variations between different growing seasons, long-term trends and further elucidate impacts of nutrient rich flood events on GHG exchange. There is a current Defra funded project (SP1210) into evaluating GHG fluxes in lowland peatland systems over a 3 year period, quantifying GHG exchange in lowland fens in the Cambridgeshire fens and Somerset levels. However, within these sites, only one of the Cambridgeshire fens sites is a site under conservation management and there is not comparison with other sites of differing nutrient status. Pre- and succeeding pore-, river and ditch water nutrient concentrations could be taken when a flood event is anticipated, as well as GHG exchange to fully ascertain the impacts of flooding events on GHG exchange.

A further long-term study should also include ditch evasion rates within the annual GHG balance. A greater number of ditch replicates would be needed than within this study to achieve more reliable ditch flux estimates. As ditches are important for water level maintenance within floodplain fens, it is important to fully understand how these environments function and how to limit GHG emissions via evasion. The impacts of flood events on GHG evasion rates could also be incorporated into a long-term study and have not previously been investigated in floodplain fens. Flood events in January and March 2013 altered CO_2 exchange (section 4.2.3) and CH_4 emissions (section 5.2.3) differently within this study. Flood dynamics on GHG evasion needs further investigation to fully understand how flooding may alter GHG emissions.

Ebullitive fluxes should also be further researched within floodplain fens in a long-term study to better understand the transport process and the controlling factors on ebullition events. A greater number of replicates could be used than within this study to better capture spatial variability in ebullition. Due to the nature of the transport mechanism, ebullition is highly spatially variable. Other studies have shown both hot and ‘cold’ spots for ebullition (Stamp et al., 2013), although this was not observed in this study. Small number of replicates may not efficiently capture a representative flux and could result in

an under- or overestimation in fluxes. Ebullition rates should also be calculated over short (~ 48 hour) time periods as this provides more reliable flux estimates (as shown in this study). If understanding on the controlling mechanisms for episodic ebullition is improved, it could be modelled to ascertain an annual flux and be incorporated into site GHG budgets.

8.2.2 Ditch and pond evasion rates in floodplain fens

This study showed significantly greater CH_4 evasion from ditches than diffusive fluxes in the two fens. A more in depth study is needed into both CO_2 and CH_4 evasion rates from fen surface water bodies to try to establish temporal and spatial variability of fluxes, as well as the controlling factors on evasion rates in ditches and ponds. To date, relatively few studies have quantified GHG evasion rates from floodplain fen ditches and have mostly had very few numbers of replicates. In Vermaat et al. (2011), ditch peat properties were investigated for nutrient contents. This could also be incorporated into a study to ascertain if nutrient contents and other substrate properties impact on evasion rates. Additionally, none of the published studies quantified CH_4 ebullition despite observing bubbles rising to the surface in the field campaign. Considering the magnitude of ebullition fluxes within the fens in this study, ditch ebullition fluxes could be considerable. Methodological issues would need to be overcome, such as stabilising a funnel to capture ebullition bubbles, to be able to quantify ditch ebullition. Currently, there are no other current studies quantifying GHG evasion within floodplain fens, despite their importance for C emissions. The findings could be used to help manage sites and inform site managers on ratios of surface water bodies to fenland to help reduce emissions.

8.2.3 Small spatial scale variation in episodic ebullition

Episodic ebullition was shown to be an important transport mechanism within this study (section 5.2.2), with fluxes the same order of magnitude as diffusive and plant-mediated transport. Rates of ebullition were also highly spatially and temporally variable, as corroborated with other studies (Stamp et al., 2013). It is well known that biogeochemical cycles are highly spatially heterogeneous (Bridgham et al., 2013), which will affect methanogenesis and potentially CH_4 release via ebullition. A study into small spatial scale variations in ebullition would help to improve the understanding of the process and improve C dynamics models.

8.2.4 Mesocosm fertilisation study on potential GHG exchange

Findings from chapter 6 helped to elucidate short-term (< 15 days) alterations to potential GHG production with NO_3^- and SRP additions. However, no vegetation was included within the microcosm experiment. As plants play a large role in GHG exchange in both the production of gases (section 2.3.1) and transport to the atmosphere (section 2.3.2), to gain a better understanding of short-term (< 15 days) alterations to GHG exchange with N and P additions a mesocosm experiment could be conducted, using peat cores and intact vegetation. The inclusion of vegetation within the mesocosm allows for the measurement of both potential CO_2 emissions and uptake via GPP. At present, no study has quantified potential CO_2 and CH_4 exchange in a controlled mesocosm experiment with N and P fertilisation. A number of mesocosm studies have quantified GHG exchange in low lying vegetation (Dinsmore et al., 2009, Green and Baird, 2012, Green et al., 2014, Yu et al., 2014). Methods used within these studies could be incorporated to a research design for tall vegetation, such as *P. australis*, to ensure that aboveground biomass is not cut to fit within the chamber to measure GHG exchange. Cutting of vegetation can induce greater GHG emissions and are not representative of the system being studied (Chanton, 2005). Results would help to complete the picture of how nutrient loading via fluvial inundation alters GHG exchange within floodplain fens.

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Appendices

Appendix 1: Sutton Fen vegetation survey

Herbaceous plants and bryophyte composition and abundance and average plant height at Sutton Fen (Domin scale – 1 to 9) measured in triplicate quadrats around each collar in September 2012 by Dr Ander Skinner (RSPB ecologist)

Species	1.1	1.2	1.3	2.1	2.2	2.3	3.1	3.2	3.3	4.1	4.2	4.3	5.1	5.2	5.3	6.1	6.2	6.3
Agrostis stolonifera				4		1					1			1	2			
Berula erecta			1	1			3	3	2		1	4	2	3	4	3	2	2
Calamagrostis canescens	2	4	4		5		4	4	5	5	1	3	4	3		1		
Cardamine spp.	1	1	1	1	1					1	1	1	1	1	1		1	1
Carex appropiriquita	1		1											3	1			
Carex elata										5	1	3						5
Carex lasiocarpa											1		2			1	2	1
Carex pseudocyperus				1	1	1	2	2	1	3	1	6	2	4	5	5	5	4
Carex spp.				1				1					1		1	1		
Carex viridula aqq.															1			
Cladium mariscus											3	1	1					
Cirsium palustre		1																
Eleocharis palustris				1		2												
Epilobium palustre			1					1										
Epilobium parviflorum		1			1		1										1	
Equisetum fluviatile	1																	

Eupatorium cannibinum							1				1					1		1
Filipendula ulmaria							2											
Galium palustre	2	2	4	2	2	1	1	2	1	3	3	1	1	1	1	2	1	2
Galium uliginosum							1		3									
Holcus lanatus	1	3	2															
Hydrocotyle vulgaris					2					1	1				1		1	1
Juncus articulatus						1											2	
Juncus subnodulosus	3	5	3	4	1	3	7	4	6	1	1	1	1	1		4	5	3
Lycopus europaeus		1	1		1		1	1		1				1		1	1	1
Lysimachia nummularia																		
Lysimachia vulgaris	1	4	3				3	3	4	4	4	3	3	2	5			3
Lythrum salicaria			1	1		1				1	1	1				2	1	1
Mentha aquatica	3	3	3	1			5	6	3	6	4	1	2	1	1	7	6	4
Myosotis laxa			1				1	1	1		1		1	1	2	1	1	1
Myrica gale		3	1		7		2		5	8	4	1				4		
Oenanthe fistulosa	1			1		1	1	1	2	1	1	1	1	1	2	1	1	2
Pedicularis palustris	5	7	5	1		4	4	3		1	5		2	1		1	2	
Peucedanum palustre				1			1		2	4								
Phalaris arundinacea																		
Phragmites australis	1	4	5	5	1		5	5	5	4	5	8	4	4	6	5	6	5
Potamogeton coloratus												7	5	5	7	1	4	2
Ranunculus lingua			1											1				
Ranunculus flammula		1														1		
Rumex conglomeratus									1							1		
Salix spp.	2		1				1		1			1				2		
Samolus valerandi																1	2	

Scutellaria galericulata	1		2																1
Sium latifolia						1			1	1	1			1	3	1	2	1
Stellaria palustris	1		1																
Thelypteris palustris	8		8	8		7	3	4	5	5	3	4	7	8	7			2
Typha latifolia																	1	
Utricularia vulgaris											6	1		3	4	2	5	2
Bryophytes	7	9	9	5	8	7	7	5	5	4		1	2	4		1		
Average vegetation height (cm)	45	63	45	81	52	45	94	67	100	59	70	87	50	64	76	93	81	75

Appendix 2: Strumpshaw Fen vegetation survey

Herbaceous plants and bryophyte composition and abundance and average plant height at Strumpshaw Fen (Domin scale – 1 to 9) measured in triplicate quadrats around each collar in September 2012 by Dr Ander Skinner (RSPB ecologist).

Species	1.1	1.2	1.3	2.1	2.2	2.3	3.1	3.2	3.3	4.1	4.2	4.3	5.1	5.2	5.3	6.1	6.2	6.3
Agrostis stolonifera				1		1				1	4	5		5	5	7	5	6
Angelica sylvestris			1															
Berula erecta					8	4		4				5		5				
Calamagrostis canescens		1						6	1				4		4	1	4	
Calystegia sepium							2		2	1						1	1	
Cardamine spp.			1			1				1	1	1			1	1	1	1
Carex acutiformis	2																	
Carex elata	7	5	6	7		1			5	8			6		1		4	1
Carex lasiocarpa													1		1			
Carex paniculata											3							
Carex riparia	1	3	1	1	2	1								4	4			
Cicuta virosa				2														
Epilobium palustre						1								1		1		
Epilobium parviflorum													1					
Eupatorium cannibinum	1	2	7	5		5	4	1	1		2		5	6	4	2		2
Filipendula ulmaria													2					
Galium palustre	5	5	2	6	4	5	2	7	2	5	4	5	4	5	6	7	6	3
Iris pseudacorus		1															1	
Juncus subnodulosus				1									3					
Lathyrus palustris		1			2			2	3					2	3		2	

Lemna minora	2	1	1		5	4	1		3	5	3	4	7				1	2
Lemna trisulca	1																	
Lycopus europaeus				1		1			5		1		1			5		
Lysimachia vulgaris		1	1	1			1	2					5	3	2	4	3	1
Lythrum salicaria	1	1		2		1		1		2			2	2	1		2	
Mentha aquatica	3	1	1	5		1		1					2	1	1	5		3
Myosotis laxa	4	2																
Oenanthe fistulosa						1												
Pedicularis palustris																		
Peucedanum palustre	3		1	3		2	3				2	1	5	4		1		
Phalaris arundinacea																		
Phragmites australis	10	10	9	10	10	9	9	9	9	9	9	10	8	8	8	8	8	9
Ranunculus lingua	2															1	2	
Rumex hydrolapathum				1	2										1	1		
Salix spp.																	1	
Scutellaria galericulata						1	1	2						1	1			
Solanum dulcamara		1			1	1		2	1				1		1			
Stellaria palustris			5						1				2			1	1	
Thalictrum flavum														2	1	1		
Thelypteris palustris			5	4	6		7	8	6	2				1	4	6	2	3
Typha latifolia	1																	
Urtica dioica								2										
Bryophytes	4	4	5	4	4	6	6	7	4	2	9	8	5	1	1	4	1	1
Average vegetation height (cm)	149	152	131	144	151	143	172	156	153	166	165	162	126	141	135	144	149	163

Appendix 3: Sutton Fen peat descriptions

3m field core descriptions for Sutton fen based on the von Post method for degree of humification, a modified Troels-Smith method for stratification, Munsell colour chart for peat colour, and Kershaw (1997) numeric scale (0 - 4) for peat darkness, elasticity and structure (section 3.1.4)

Site: Sutton Fen Core number: 1 BNG eastings and northings: TG 36764 23156

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-26.5	26.5	H6	Th^3	3	1	2	7.5YR 2.5/2	Fibrous	
26.5-34.5	8	H6	Sh	3	0	0	7.5YR 2.5/1	Homogenous	Woody debris
34.5-49	14.5	H7	Tl^2	3	0	0	7.5YR 2.5/1	Homogenous	
49-65	16	H7	Dg	4	0	0	7.5YR 2.5/1	Homogenous	Very wet
65-72	7	H8	Dg	4	0	0	7.5YR 2.5/1	Homogenous	
72-85	13	H7	Dh	4	0	0	7.5YR 2.5/1	Homogenous	
85-125	40	H8	Dl	4	0	0	7.5YR 2.5/1	Homogenous	
125-139	14	H8	Dl	4	0	0	7.5YR 2.5/1	Homogenous	
139-186	47	H8	Dl	4	0	0	7.5YR 2.5/1	Homogenous	
186-189	3	H5	Dl	4	0	0	7.5YR 2.5/1	Homogenous	
189-239	50	H8	Dg	4	0	0	7.5YR 2.5/1	Homogenous	

239-289	50	H8	Ld[1]	4	0	0	7.5YR 2.5/1	Homogenous
289-300	11	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous

Site: Sutton Fen Core number: 2 BNG eastings and northings: TG 36755 23165

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0–30	30	H3	Th[2]	3	0	1	7.5YR 2.5/3	Fibrous	
30-68	38	H8	Dg	4	0	0	7.5YR 2.5/1	Fibrous	Herb. Plant remains
68-81	13	H9	Ld[2]	4	0	0	7.5YR 2.5/1	Homogenous	
81-91	10	H9	Ld[2]	4	0	0	7.5YR 2.5/1	Homogenous	
91-131	40	H7	Tl4	3	0	0	7.5YR 2.5/1	Fibrous	Woody
131-166	35	H7	Dl	4	0	0	7.5YR 2.5/1	Homogenous	Large woody detritus
166-216	50	H6	Dg_{woody}	3	0	0	7.5YR 2.5/1	Homogenous	
216-266	50	H6	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
266-316	60	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/1	Fibrous	

Site: Sutton Fen Core number: 3 BNG eastings and northings: TG 36755 23173

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-45	45	H5	Th^3	2	0	0	7.5YR 4/3	Fibrous	
45-95	50	H7	Th^3	3	0	0	7.5YR 2.5/3	Fibrous	
95-145	50	H8	Th^3	3	0	0	7.5YR 2.5/3	Fibrous	
145-195	50	H8	Th^3	3	0	0	7.5YR 2.5/3	Fibrous	
195-245	50	H8	Th^0	4	0	0	7.5YR 2.5/3	Homogenous	
245-300	55	H8	Sh	4	0	0	7.5YR 2.5/3	Homogenous	Small parts of woody debris

Site: Sutton Fen Core number: 4 BNG eastings and northings: TG 36753 23173

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-50	50	H5	TH^3	3	0	1	7.5YR 3/3	Fibrous	
50-83	33	H5	$Dg_{herbaceous}$	3	0	1	7.5YR 3/3	Fibrous	
53-133	50	H5	$Dg_{herbaceous}$	3	0	1	7.5YR 3/3	Fibrous	
133-183	50	H5	$Dg_{herbaceous}$	3	0	1	7.5YR 3/3	Fibrous	
183-207	24	H5	$Dg_{herbaceous}$	3	0	1	7.5YR 3/3	Fibrous	
207-235	28	H7	Dl	3	0	1	7.5YR 3/3	Fibrous	
235-285	50	H7	Sh	3	0	1	7.5YR 3/3	Fibrous	
285-300	15	H7	Sh	3	0	1	7.5YR 3/3	Fibrous	

Site: Sutton Fen Core number: 5 BNG eastings and northings: TG 36752 23166

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-43	43	H5	Th^2	4	0	0	7.5YR 2.5/2	Fibrous	
43-93	50	H5	Th^1	4	0	0	7.5YR 2.5/2	50:50	
93-143	50	H6	Ld^2	4	0	0	7.5YR 2.5/2	Homogenous	
143-193	50	H6	Ld^2	4	0	0	7.5YR 2.5/2	Homogenous	
193-228	35	H10	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
228-243	15	H10	Sh	4	0	0	7.5YR 2.5/2	Homogenous	Small amount of woody debris < 2 mm
243-300	57	H10	Sh	4	0	0	7.5YR 2.5/2	Homogenous	

Site: Sutton Fen Core number: 6 BNG eastings and northings: TG 36747 23170

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-50	50	H5	Th^2	2	0	0	7.5YR 4/4	Homogenous	
50-89	39	H7	Dh	3	0	0	7.5YR 2.5/2	Homogenous	
89-100	11	H8	Dh	3	0	0	7.5YR 2.5/2	Homogenous	
100-150	50	H8	Dh	3	0	0	7.5YR 2.5/1	Homogenous	
150-200	50	H8	Dh	3	0	0	7.5YR 2.5/1	Homogenous	
200-250	50	H8	Sh	3	0	0	7.5YR 2.5/1	Homogenous	
250-300	50	H8	Sh	3	0	0	7.5YR 2.5/1	Homogenous	

Site: Sutton Fen Core number: 7 BNG eastings and northings: TG 36741 23176

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-50	50	H5	Th^2	4	0	0	7.5YR 2.5/1	50:50	
50-100	50	H5	Th^2	4	0	0	7.5YR 2.5/1	50:50	
100-150	50	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/1	Homogenous	
150-200	50	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/1	Homogenous	
200-221	21	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/1	Homogenous	
221-250	29	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/1	50:50	
250-300	50	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/1	Homogenous	

Site: Sutton Fen Core number: 8 BNG eastings and northings: TG 36743 23160

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-50	50	H8	Th^3	3	0	0	7.5YR 2.5/2	Fibrous	
50-100	50	H8	Th^3	3	0	0	7.5YR 2.5/2	Fibrous	
100-150	50	H7	Th^3	3	0	0	7.5YR 2.5/2	Fibrous	
150-200	50	H7	Th^3	3	0	0	7.5YR 2.5/2	Fibrous	
200-220	20	H8	Th^3	3	0	0	7.5YR 2.5/2	Fibrous	
220-250	30	H7	Th^3	3	0	0	7.5YR 2.5/2	Fibrous	
250-300	50	H7	Th^3	3	0	0	7.5YR 2.5/2	Fibrous	Small amounts of woody debris

Site: Sutton Fen Core number: 9 BNG eastings and northings: TG 36745 23154

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-50	50	H5	Th^0	4	0	0	7.5YR 2.5/1	Fibrous	Small amounts of woody debris
50-100	50	H5	Th^0	4	0	0	7.5YR 2.5/1	Fibrous	
100-110	10	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
110-150	40	H5	Dg_{woody}	4	0	0	7.5YR 2.5/1	Homogenous	
150-200	50	H5	Dg_{woody}	4	0	0	7.5YR 2.5/1	Homogenous	
200-250	50	H5	Dg_{both}	4	0	0	7.5YR 2.5/1	Homogenous	
250-300	50	H5	Tl^3	4	0	0	7.5YR 2.5/1	Homogenous	

Site: Sutton Fen Core number: 10 BNG eastings and northings: TG 36741 23147

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-45	45	H4	Th^2	4	0	0	7.5YR 2.5/2	Fibrous	
45-95	50	H4	Th^2	4	0	0	7.5YR 2.5/2	Fibrous	
95-145	50	H5	Th^2	4	0	0	7.5YR 2.5/2	Homogenous	
145-195	50	H5	Th^2	4	0	0	7.5YR 2.5/2	Homogenous	
195-213	18	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/2	Homogenous	
213-245	32	H6	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/2	Homogenous	
245-300	55	H6	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/2	Homogenous	

Site: Sutton Fen Core number: 11 BNG eastings and northings: TG 36737 23155

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-30	30	H5	Th^{3}	4	0	0	7.5YR 3/2	Fibrous	
30-50	20	H7	$Dg_{herbaceous}$	4	0	0	7.5YR 4/3	Homogenous	
50-63	13	H7	$Dg_{herbaceous}$	4	0	0	7.5YR 4/3	Homogenous	
63-100	37	H7	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/1	Homogenous	
100-150	50	H7	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/1	Homogenous	
150-200	50	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/1	Homogenous	
200-250	50	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/1	Homogenous	
250-300	50	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/1	Homogenous	

Site: Sutton Fen Core number: 12 BNG eastings and northings: TG 36734 23171

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-18	18	H4	Th^{4}	4	0	0	7.5YR 3/3	Fibrous	
18-40	22	H5	Th^{4}	3	0	0	7.5YR 5/6	Fibrous	
40-50	10	H6	Th^{2}	4	0	0	7.5YR 2.5/2	50:50	
50-100	50	H6	Th^{2}	4	0	0	7.5YR 2.5/2	75:25	
100-150	50	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/2	Homogenous	
150-200	50	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/2	Homogenous	
200-250	50	H8	Ld^{1}	4	0	0	7.5YR 2.5/2	Homogenous	Very wet and sloppy
250-300	50	H8	Ld^{1}	4	0	0	7.5YR 2.5/2	Homogenous	

Site: Sutton Fen Core number: 13 BNG eastings and northings: TG 36728 23166

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-50	50	H6	Th^{2}	4	0	0	7.5YR 2.5/3	Fibrous	
50-100	50	H6	Th^{2}	4	0	0	7.5YR 2.5/3	Fibrous	
100-150	50	H6	Th^{1}	4	0	0	7.5YR 2.5/3	Fibrous	
150-200	50	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/3	Fibrous	
200-250	50	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/3	Homogenous	
250-300	50	H10	Sh	4	0	0	7.5YR 2.5/3	Homogenous	

Site: Sutton Fen Core number: 14 BNG eastings and northings: TG 36731 23156

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-50	50	H6	$Dg_{herbaceous}$	2	0	0	7.5 2.5/3	50:50	
50-70	20	H6	$Dg_{herbaceous}$	2	0	0	7.5 2.5/3	50:50	
70-120	50	H8	$Dg_{herbaceous}$	3	0	0	7.5 2.5/3	Homogenous	
120-170	50	H8	$Dg_{herbaceous}$	4	0	0	7.5 2.5/3	Homogenous	Some woody detritus
170-220	50	H8	Dg_{woody}	4	0	0	7.5 2.5/3	Homogenous	
220-270	50	H8	$Dg_{herbaceous}$	4	0	0	7.5 2.5/3	Homogenous	
270-300	30	H8	$Dg_{herbaceous}$	4	0	0	7.5 2.5/3	Homogenous	

Site: Sutton Fen Core number:15 BNG eastings and northings: TG 36739 23134

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-50	50	H5	Th^{2}	4	0	0	7.5YR 2.5/2	Fibrous	
50-100	50	H7	Th^{2}	4	0	0	7.5YR 2.5/2	50:50	
100-150	50	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/2	50:50	
150-200	50	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/2	Homogenous	
200-250	50	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/2	Homogenous	Woody detritus
250-300	50	H8	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/2	Homogenous	

Appendix 4: Strumpshaw Fen peat descriptions

3m field core descriptions for Sutton fen based on the von Post method for degree of humification, a modified Troels-Smith method for stratification, Munsell colour chart for peat colour, and Kershaw (1997) numeric scale (0 - 4) for peat darkness, elasticity and structure (section 3.1.4)

Site: Strumpshaw Fen Core number: 1 BNG eastings and northings: TG 33590 07075

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-6	6	H5	Th^{2}	4	0	0	7.5YR 2.5/2	Fibrous	
6-50	44	H5	Th^{3}	4	0	0	7.5YR 2.5/2	Fibrous	
50-90	40	H5	Th^{3}	4	0	0	7.5YR 2.5/2	Fibrous	
90-112	22	H8	Ld^{3}	4	0	0	7.5YR 2.5/2	Homogenous	Very sloppy
112-140	28	H6	$Dg_{herbaceous}$	4	0	0	7.5YR 2.5/2	Homogenous	
140-190	50	H8	Ld^{3}	4	0	0	7.5YR 2.5/2	Homogenous	
190-240	50	H8	Ld^{3}	4	0	0	7.5YR 2.5/2	Homogenous	
240-300	60	H8	Ld^{3}	4	0	0	7.5YR 2.5/2	Homogenous	

Site: Strumpshaw Fen Core number: 2 BNG eastings and northings: TG 33589 07077

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-9	9	H6	Th^2	4	0	0	7.5YR 2.5/2	50:50	
9-50	41	H5	Th^2	4	0	0	7.5YR 2.5/2	50:50	
50-67	17	H5	Th^2	4	0	0	7.5YR 2.5/2	50:50	
67-100	33	H8	Ld^3	4	0	0	7.5YR 2.5/2	Homogenous	
100-150	50	H8	Ld^3	4	0	0	7.5YR 2.5/2	Homogenous	
150-200	50	H9	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
200-250	50	H9	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
250-300	50	H9	Sh	4	0	0	7.5YR 2.5/2	Homogenous	

Site: Strumpshaw Fen Core number: 3 BNG eastings and northings: TG 33591 07078

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-17	17	H6	Th[2]	4	0	0	7.5YR 2.5/2	50:50	
17-50	33	H8	Ld[3]	4	0	0	7.5YR 2.5/2	Homogenous	
50-69	19	H8	Ld[3]	4	0	0	7.5YR 2.5/2	Homogenous	
69-100	31	H8	Dh	4	0	0	7.5YR 2.5/2	Homogenous	
100-150	50	H9	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
150-200	50	H9	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
200-250	50	H9	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
250-300	50	H9	Sh	4	0	0	7.5YR 2.5/2	Homogenous	

Site: Strumpshaw Fen Core number: 4 BNG eastings and northings: TG 33596 07069

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-8	8	H4	Dh	4	0	0	7.5YR 2.5/1	50:50	
8-18	10	H8	Th^3	4	0	0	7.5YR 2.5/1	50:50	
18-50	32	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
50-100	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
100-150	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
150-200	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
200-250	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
250-300	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	

Site: Strumpshaw Fen Core number: 5 BNG eastings and northings: TG 33598 07065

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-10	10	H3	Th[4]	3	0	0	7.5YR 2.5/3	Homogenous	
10-50	40	H9	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
50-100	50	H9	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
100-150	50	H9	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
150-200	50	H9	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
200-250	50	H9	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
250-300	50	H9	Sh	4	0	0	7.5YR 2.5/2	Homogenous	

Site: Strumpshaw Fen Core number: 6 BNG eastings and northings: TG 33598 07065

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-7	7	H5	Dh	4	0	0	7.5YR 2.5/2	Fibrous	Dead culms
7-16	9	H5	Dh	4	0	0	7.5YR 2.5/3	Fibrous	
16-20	4	H4	Dh	4	0	0	7.5YR 2.5/2	Fibrous	
20-30	10	H8	Th^4	4	0	0	7.5YR 2.5/2	50:50	Sloppy but dense root mat
30-50	20	H8	Th^4	4	0	0	7.5YR 2.5/2	Homogenous	
50-100	50	H8	Th^4	4	0	0	7.5YR 2.5/2	Homogenous	
100-150	50	H8	Th^4	4	0	0	7.5YR 2.5/2	Homogenous	
150-200	50	H8	Th^4	4	0	0	7.5YR 2.5/2	Homogenous	
200-250	50	H8	Th^4	4	0	0	7.5YR 2.5/2	Homogenous	
250-300	50	H8	Th^4	4	0	0	7.5YR 2.5/2	Homogenous	

Site: Strumpshaw Fen Core number: 7 BNG eastings and northings: TG 33571 07060

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-10	10	H5	Th^4	4	0	0	7.5YR 2.5/1	Fibrous	
10-50	40	H9	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
50-100	50	H9	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
100-150	50	H9	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
150-200	50	H9	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
200-250	50	H9	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
250-300	50	H9	Sh	4	0	0	7.5YR 2.5/1	Homogenous	

Site: Strumpshaw Fen Core number: 8 BNG eastings and northings: TG 36743 23160

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-15	15	H4	Th^4	3	0	0	7.5YR 2.5/2	Fibrous	
15-25	20	H5	Th^2	4	0	0	7.5YR 2.5/2	50:50	
25-50	25	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
50-100	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
100-150	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
150-200	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
200-250	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
250-300	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	

Site: Strumpshaw Fen Core number: 9 BNG eastings and northings: TG 33572 07059

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-20	20	H5	Th[1]	3	0	0	7.5YR 2.5/2	Fibrous	
20-50	30	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
50-100	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
100-150	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
150-200	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
200-250	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
250-300	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	

Site: Strumpshaw Fen Core number: 10 BNG eastings and northings: TG 3363107028

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour0702 8 (Munsell chart)	Structure	Comments
0-10	10	H5	Th[1]	3	0	0	7.5YR 2.5/2	Fibrous	
10-50	40	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
50-100	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
100-150	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
150-200	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
200-250	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
250-300	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	

Site: Strumpshaw Fen Core number: 11 BNG eastings and northings: TG 33632 07025

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-20	20	H5	Th^4	3	0	0	7.5YR 2.5/2	Fibrous	
20-50	30	H8	Dh	3	0	0	7.5YR 2.5/2	Homogenous	
50-100	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
100-150	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
150-200	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
200-250	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
250-300	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	

Site: Strumpshaw Fen Core number: 12 BNG eastings and northings: TG 33631 07025

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-20	20	H5	Th^3	4	0	0	7.5YR 2.5/2	Fibrous	
20-50	30	H8	Dh	4	0	0	7.5YR 2.5/2	50:50	
50-100	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
100-150	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
150-200	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
200-250	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	
250-300	50	H8	Sh	4	0	0	7.5YR 2.5/2	Homogenous	

Site: Strumpshaw Fen Core number: 13 BNG eastings and northings: TG 33640 07026

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-30	30	H6	Dh	4	0	0	7.5YR 2.5/1	50:50	
30-50	20	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
50-100	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
100-150	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
150-200	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
200-250	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
250-300	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	

Site: Strumpshaw Fen Core number: 14 BNG eastings and northings: TG

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-4	4	H4	Th^4	3	0	0	7.5YR 5/1	Fibrous	
4-24	20	H8	Dg	4	0	0	7.5YR 2.5/1	Homogenous	
24-50	26	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
50-100	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
100-150	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
150-200	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
200-250	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
250-300	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	

Site: Strumpshaw Fen Core number:15 BNG eastings and northings: TG 33648 07022

Depth from surface (cm)	Length of section (cm)	Humification (von Post)	Botanical composition	Degree of darkness	Degree of stratification	Degree of elasticity	Colour (Munsell chart)	Structure	Comments
0-40	40	H8	Th[1]	4	0	0	7.5YR 2.5/1	Homogenous	
40-100	60	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
100-150	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
150-200	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
200-250	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	
250-300	50	H8	Sh	4	0	0	7.5YR 2.5/1	Homogenous	

Appendix 5: Correspondence analysis species names and results.

Plant species followed the following naming system for correspondence analysis; the first three letters of the species, followed by the first three letters of the subspecies. The table below outlines all species and the names used:

Species	CA name
Agrostis stolonifera L. (1753)	Agr.sto
Berula erecta (Huds.) Coville (1893)	Ber.ere
Calamagrostis canescens L. (Weber) Roth (1789)	Cal.can
Cardamine spp.	Car.spp
Carex acutiformis Ehrh. (1789)	Car.acu
Carex appropinquata Schumach. (1801)	Car.app
Carex elata All. (1785)	Car.ela
Carex pseudocyperus L. (1753)	Car.pse
Carex riparia Curtis (1783)	Car.rip
Carex spp.	Car.spp
Calystegia sepium (L.) R. Br. (1810)	Cal.sep
Cladium mariscus (L.) Pohl (1809)	Cla.mar
Cirsium palustre (L.) Coss. ex Scop. (1772)	Cir.pal
Epilobium palustre L. (1753)	Epi.pal
Epilobium parviflorum Schreb. (1771)	Epi.par
Eupatorium cannabinum L. (1753)	Eup.can
Galium palustre L. (1753)	Gal.pal
Holcus lanatus L. (1753)	Hol.lan
Hydrocotyle vulgaris L. (1753)	Hyd.vul
Iris pseudacorus L. (1753)	Iri.pse
Juncus articulatus L. (1753)	Jun.art
Juncus subnodulosus Schrank (1789)	Jun.sub
Lathyrus palustris L. (1753)	Lat.pal
Lemna minor L. (1753)	Lem.min
Lychnis flos-cuculi L. (1753)	Lyc.flo
Lycopus europaeus L. (1753)	Lyc.eur
Lysimachia nummularia L. (1753)	Lys.num
Lysimachia vulgaris L. (1753)	Lys.vul
Lythrum salicaria L. (1753)	Lyt.sal
Mentha aquatica L. (1753)	Men.aqu
Myosotis laxa Lehm. (1818)	Myo.lax
Oenanthe fistulosa L. (1753)	Oen.fis
Pedicularis palustris L. (1753)	Ped.pal
Peucedanum palustre (L.) Moench (1794)	Peu.pal
Phalaris arundinacea L. (1753)	Pha.aru
Phragmites australis (Cav.) Trin. ex Steud. (1841)	Phr.aus
Potamogeton coloratus Hornem. (1813)	Pot.col
Ranunculus lingua L. (1753)	Ran.lin
Salix spp.	Sal.spp
Scutellaria galericulata L. (1753)	Scu.gal
Sium latifolium L. (1753)	Siu.lat
Solanum dulcamara L. (1753)	Sol.dul
Sonchus palustris L. (1753)	Son.pal
Stellaria palustris Ehrh. ex Retz. (1795)	Ste.pal
Thelypteris palustris Schott (1834)	The.pal
Typha latifolia L. (1753)	Typ.lat
Bryophytes	Bry.

Results from the CA are in the following table:

	CA1	CA2	CA3	CA4	CA5	CA6	CA7	CA8	CA9	CA10	CA11
Eigenvalue	0.404	0.352	0.328	0.250	0.193	0.191	0.144	0.110	0.085	0.057	0.035
Proportion explained	0.188	0.164	0.153	0.116	0.090	0.090	0.067	0.051	0.040	0.0266	0.0162
Cumulative proportion	0.188	0.352	0.504	0.621	0.711	0.80	0.867	0.912	0.957	0.984	1.00

Appendix 6: Microcosm pilot study

The anaerobic microcosm method was trialled using a pilot study, undertaken on peat taken in November 2013, as detailed in section 6.2.2 and processed as in section 6.2.3. Briefly, 30 surface samples (top 0 – 10 cm) were taken randomly from the areas delineated by greenhouse gas (GHG) exchange monitoring under R.Q. 2 to R.Q. 4 (section 3.1.3) within both Sutton and Strumpshaw Fen, respectively. Sample bags were filled as much as possible, removing as much excess air to create anoxic conditions, and double bagged to reduce O_2 diffusion. Samples were then processed in the laboratory within anaerobic conditions, where the substrate was pooled per site and then passed through a 0.2 mm sieve to remove roots and rhizomes. Water content was calculated using Eq. 23 and 24. Peat, 2.4 and 2.8 g wet weight corresponding to 2 g dry weight, was weighed into 50 mL serum bottles and were sealed with a butyl rubber stopper and crimped shut. Serum bottles were wrapped in foil to prevent any light penetration into the serum bottle. The serum bottles were flushed with oxygen free nitrogen (OFN) for 20 minutes and pre-incubated for 3 days at 16 °C.

Triplicate control (deoxygenated ultrapure water; UHQ) and fertilised samples (fertilisation solution made up of final concentrations of 51 mg L^{-1} NO_3^- and 1.4 mg L^{-1} PO_4^{3-}) were used, as well as a single glucose sample (fertilised with 1000 mg L^{-1} glucose; total n = 7 per site). UHQ, fertilisation and glucose solutions were deoxygenated for 30 minutes using OFN. As outlined in section 6.2.4 and 6.2.5, after the pre-incubation period, serum bottles were flushed with OFN for 20 minutes and then the UHQ, fertilisation solution or glucose was added to the control, fertilised and glucose samples, respectively, for Sutton and Strumpshaw Fen peat samples. Samples were shaken and left for an hour before taking a headspace sample. The 0.6 mL gas headspace was injected into a 3 mL exetainer filled with a deoxygenated saline solution (58 mg L^{-1}), allowing the excess 0.6 mL solution to flow out through a secondary needle. Headspace samples were then taken at 25, 49, 73, 97, 121, 145, 193 and 256 hours, shaking the serum bottles prior to taking a headspace sample. Samples were analysed as in section 6.2.5. Results are shown below in Figure 96.

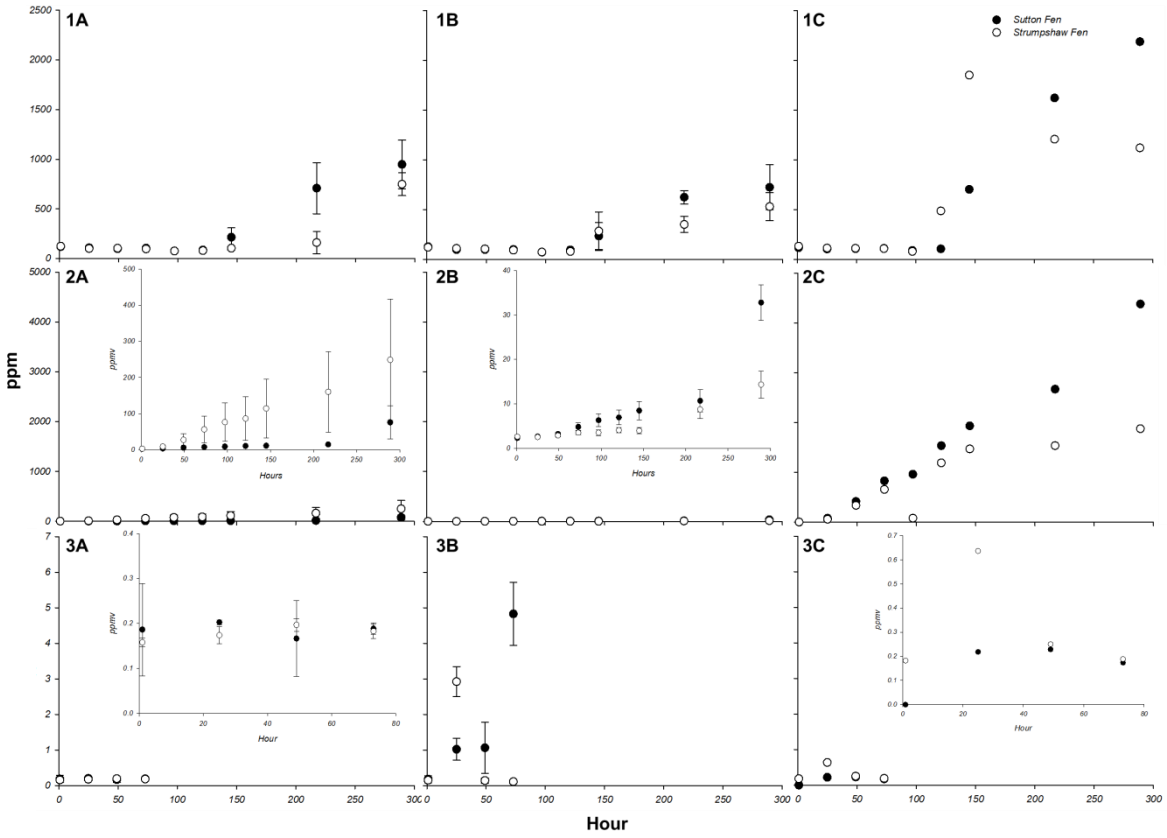

Figure 96 Pilot microcosm results for potential (1) CO_2, (2) CH_4 and (3) N_2O production in (A) unfertilised, (B) fertilised and (C) glucose addition samples.

The unclear responses in fertilised samples were caused due to the combination of both N and P in the fertilisation solution and did not allow for the elucidation of alterations to potential GHG production with the two different macronutrients. Additionally, the very small amounts of potential CH_4 production in comparison to glucose additions (Figure 96 2C) led to the assumption that the samples were labile C poor and that the addition of glucose to the samples should be included to help show normal functioning of the substrates, which otherwise would receive labile C from root exudates, and alterations to potential GHG production. In a flood event, labile C would be also added to the fens via DOC, which could be used readily by microbial populations for fermentation, methanogenesis and denitrification.